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ABBREVIATIONS

aq. = aqueous

atm. = atmospheric or atmosphere(s)

at. vol. = atomic volume(s)

at. wt. = atomic weight(s)

T° or °K = absolute degrees of temperature

b.p. = boiling point(s)

$\vartheta°$ = centigrade degrees of temperature

coeff. = coefficient

conc. = concentrated or concentration

dil. = dilute

eq. = equivalent(s)

f.p. = freezing point(s)

m.p. = melting point(s)

mol(s) = {gram-molecule(s) / gram-molecular

mol(s). = {molecule(s) / molecular

mol. ht. = molecular heat(s)

mol. vol. = molecular volume(s)

mol. wt. = molecular weight(s)

press. = pressure(s)

sat. = saturated

soln. = solution(s)

sp. gr. = specific gravity (gravities)

sp. ht. = specific heat(s)

sp. vol. = specific volume(s)

temp. = temperature(s)

vap. = vapour

In the **cross references** the first number in clarendon type is the number of the volume; the second number refers to the chapter; and the succeeding number refers to the "§," section. Thus **4**, 31, 33 refers to § 33, chapter 31, volume 4.

The oxides, hydrides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates are considered with the basic elements; the other compounds are taken in connection with the acidic element. The double or complex salts in connection with a given element include those associated with elements previously discussed. The carbides, silicides, titanides, phosphides, arsenides, etc., are considered in connection with carbon, silicon, titanium, etc. The intermetallic compounds of a given element include those associated with elements previously considered.

The use of **triangular diagrams** for representing the properties of three-component systems was suggested by G. C. Stokes (*Proc. Roy. Soc.*, **49**. 174, 1891). The method was immediately taken up in many directions and it has proved of great value. With practice it becomes as useful for representing the properties of ternary mixtures as squared paper is for binary mixtures. The principle of triangular diagrams is based on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is a constant. Given any three substances *A*, *B*, and *C*, the composition of any possible combination of these can be represented by a point in or on the triangle. The apices of the

triangle represent the single components A, B, and C, the sides of the triangle represent binary mixtures of A and B, B and C, or C and A; and points within the triangle ternary mixture. The compositions of the mixtures can be represented in percentages, or referred to unity, 10, etc. In Fig. 1, pure A will be represented by a point at the apex marked A. If 100 be the

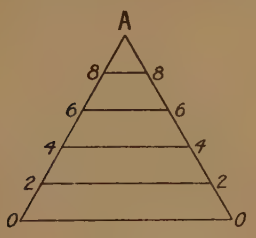

Fig. 1.

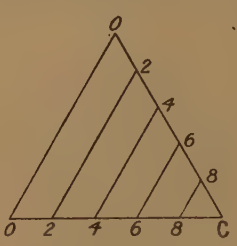

Fig. 2.

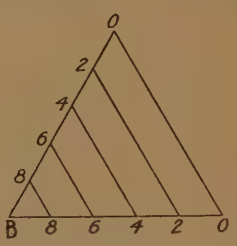

Fig. 3.

standard of reference, the point A represents 100 per cent. of A and nothing else; mixtures containing 80 per cent. of A are represented by a point on the line 88, 60 per cent. of A by a point on the line 66, etc. Similarly with B and C—Figs. 3 and 2 respectively. Combine Figs. 1, 2, and 3 into one diagram by superposition, and Fig. 4 results. Any point in this

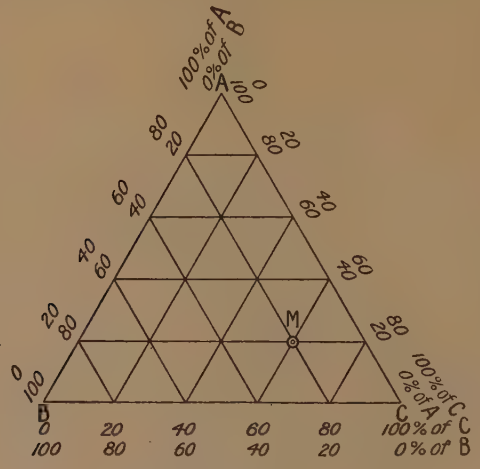

Fig. 4.—Standard Reference. Triangle.

diagram, Fig. 4, thus represents a ternary mixture. For instance, the point M represents a mixture containing 20 per cent. of A, 20 per cent. of B, and 60 per cent. of C.

CHAPTER XXV

THE STRUCTURE OF MATTER

§ 1. The Unitary Theory of Matter

Simplicity is the seal of truth. Nature is wonderfully simple, and the characteristic mark of a childlike simplicity is stamped upon all that is true and noble in nature.—M. Sendivogius (1650).

Chemistry marches towards its goal and towards its perfection by dividing, subdividing, and subdividing still again.—A. L. Lavoisier (1789).

The properties of the different elements result from differences of arrangement arising by the composition and recomposition of ultimate homogeneous units.—H. Spencer.

Belief in the simplicity of nature is not logic but faith pure and simple. It is one of those insidious and dangerous *tacit* assumptions which often creep into scientific theories. Tacit assumptions are dangerous because they are usually made unconsciously, so that they appear to be self-evident truths, and prevent our harbouring the shadow of a doubt of their insidious character. True enough, as H. Poincaré has said: "Every generalization supposes in a certain measure a belief in the simplicity of nature . . . every law is considered to be simple until the contrary has been proved," but faith in this dogma has sometimes led men astray. In consequence, hypotheses have frequently flourished in spite of experimental evidence to the contrary. It is not at all uncommon to find that a law which appears to be quite simple, when the methods of measurement are crude and approximate, becomes exceedingly complex when more accurate data are available. We have found this to be the case, for instance, with Boyle's law, Charles' law, etc. Another example will now be given.

There was a marked tendency among the earlier Greek philosophers to postulate one single kind of matter, a **protyle**—πρώτη, earlier than, or first; ὕλη, matter, or the stuff of which the things are made—or **primal element.** This *prima materia* or potential matter was supposed to consist of parts which when grouped in different ways produced the various kinds of matter considered by them to be elemental. The hypothesis is sometimes called the **unitary theory of matter: all the different forms of matter in the universe are derived from one and the same primordial element.** The unity of matter, said G. D. Hinrichs, is as real as the unity of force.

The philosopher Anaximenes regarded air as the primal element; Herakleitos, fire; Pherekides, earth; W. Prout, hydrogen; and modern chemical philosophers, electrons, and possibly æther. Thales of Miletus, who flourished in the sixth century B.C., considered that water was the first principle. Thales' doctrine had many supporters—J. B. van Helmont (1682), etc.—it lived for nearly twenty-five centuries; and it was demolished in 1770 when A. L. Lavoisier demonstrated that water cannot be changed into earth.

In 1815 and 1816, W. Prout believed that the at. wt. of the elements were exact multiples of the at. wt. of hydrogen, so that an atom of any element must weigh a certain number of times as much as an atom of hydrogen. He said:

If the views we have endeavoured to advance be correct, we may also consider the πρώτη ὕλη of the ancients to be realized in hydrogen, an opinion, by the way, not altogether new. If we actually consider this to be the case, and further consider the sp. gr. of bodies in their gaseous state to represent the number of volumes condensed into one; or, in other

words, the number of the absolute weight of a single volume of the first matter which they contain, which is extremely probable, multiples in weight must also indicate multiples in volume, and *vice versâ* ; and the sp. gr. or absolute weights of all bodies in the gaseous state, must be multiples of the sp. gr. or absolute weight of the first matter, because all bodies in a gaseous state which unite with one another, unite with reference to their volume.

According to **Prout's hypothesis, the elements are different aggregates of the atoms of primordial hydrogen ; that is, the different elements are polymers of hydrogen ;** in consequence, within the limits of experimental error, the at. wt. of the different elements should be expressible by whole numbers when the at. wt. of hydrogen is unity.

Many writers attracted by its apparent simplicity gave unqualified support to Prout's hypothesis ; but an impartial review of the facts, with very much more refined data than were available in Prout's day, led J. S. Stas to state : " I have arrived at the absolute conviction, the complete certainty, so far as is possible for a human being to attain to certainty in such matters, that the law of Prout is nothing but an illusion, a mere speculation definitely contradicted by experience." J. C. G. de Marignac added :

If Prout's law is not strictly confirmed by experiment, it nevertheless appears to express the relation between simple bodies with sufficient accuracy for the practical calculations of the chemist, and perhaps also the normal relationship which ought to exist among these weights, when allowance is made for some perturbing causes, the research for which should exercise the capacity and imagination of chemists. Should we not, for example, be quite in keeping with the fundamental principle of the law in admitting the hypothesis of the unity of matter, if we made the following supposition to which I attach no further importance than that of showing that we may be able to explain the discordance which exists between the experimental results and the direct consequences of the principle ? May we not be able to suppose that the unknown cause (probably differing from the physical and chemical agents known to us), which has determined certain groupings of primordial matter so as to give birth to our simple chemical atoms, and to impress each of these groups with a special character and peculiar properties, has been able at the same time to exercise an influence upon the manner in which these groups of atoms obey the law of universal attraction, so that the weight of each of them is not exactly the sum of the weights of the constituent primordial atoms ?

Many have tried to reconcile W. Prout's hypothesis with facts by changing the standard of reference to an imaginary primordial element with an at. wt. eq. to half an atom of hydrogen (J. C. G. de Marignac) ; then to a quarter of an atom (J. B. A. Dumas). However, having once begun to divide the hydrogen atom, there was no limit to the process of subdivision, and the hypothesis could then be made to fit any conceivable set of at. wts. This tinkering with W. Prout's hypothesis brought it, for a time, into disfavour.

The elements, as has been said, are substances which have never been resolved into simpler substances ; it is not said that the elements will never be decomposed into a more primitive form (or forms) of matter. **The atom of an element can be defined as a substance whose parts are held together by a force superior to any which has yet been brought to bear upon it.** The elements have hitherto proved undecomposable, but it is quite conceivable that they are not absolutely undecomposable. Much circumstantial evidence has accumulated in recent years which makes it increasingly difficult to believe that Dalton's atoms are absolutely indivisible ; and to deny that all the different elements have been formed from one homogeneous simple primal form of matter. The hypothesis appears in the Hellenic philosophies, and in those of the Neo-platonists. Albertus Magnus, in his *De generatione elementorum*, said that " the first matter was not generated but created out of nothing." Roger Bacon also said in his *De arte chymiæ* (Frankfurt, 1603) :

There are four elements : fire, water, air, and earth ; that is, the properties of their condition are four : heat, cold, dryness, and wetness. *Yle* (ὕλη, matter)—the true matter—contains not heat, not cold, not dryness, not wetness. The elements are made of *yle*, and each of the other elements is converted into the nature of the other element, and everything into anything else.

Raymund Lully wrote[1] similarly in his *De materia*. He said: The *prima materia* exists *in potentia* in particular forms in all substances. The idea can also be traced under various guises through writings of the alchemists down to the present time. G. D. Hinrichs has called the *prima materia* **pantogen** (1857); W. Crookes, **protyle** (1886); and J. L. G. Meinecke, **urstoff** (1817). It has been said that protyle "is matter generalized, stripped of its distinctions, the same from whatever source derived; it is matter in potency rather than in act; intangible; inaccessible to sense perception; and probably indifferent to the solicitations of gravity."

The idea that all the different forms of matter represent different stages in the growing complexity of one single elemental form of matter, has haunted the human mind from the earliest times, and the belief that "unity is the law of God," or that *simplex veri sigillum*, has proved so peculiarly fascinating that a remarkable number of speculations have been spun about this theme. These ingenious and subtle systems are admirable works of art, but they are outside the realm of science so long as the evidence on which they are founded remains intangible and vague. In recent years still another hypothesis is claimed to have been woven with circumstantial evidence which is rather more substantial than the incomprehensible fictions of the metaphysicians, for it can be examined and tested by comparison with gross material facts. It is supposed that the elements have been developed by the condensation of a primitive form of matter; and that the different elements, as W. Crookes expresses it, have been evolved by a kind of struggle for existence where elements, not in harmony with their environment, have either disappeared—*extinct elements*—or have never existed; where elements—*asteroidal elements*—have come into being and survived only on a limited scale, as is the case with the *scarcer elements;* and where other elements predominate because the surrounding conditions have been favourable to their formation and preservation, *e.g.* the *common elements*. This circumstantial evidence can now be outlined:

1. Why do so many atomic weights approximate to whole numbers?—The International Table of Atomic Weights, 1922, contains 83 elements, and of these, 43 are integers within one-tenth of a unit. This fact has nothing to do with Prout's discarded hypothesis, but the numbers are facts which can hardly be due to chance, because the probability of this occurring is exceedingly small—something like one in 20,000 millions. Calculations have been made by J. W. Mallet,[2] and R. J. Strutt. The probability that the deviations of the first 27 elements of low at. wt. from whole numbers (oxygen 16), should be by chance as small as it is, was found by W. D. Harkins and E. D. Wilson to be one in 15,000,000. It is argued that the approximation of the at. wt. of so many elements to whole numbers cannot be reasonably attributed to a fortuitous coincidence; or, as R. J. Strutt puts it, "to use Laplace's mode of expression, we have stronger reasons for believing in the truth of some modification of Prout's law than in that of many historical events which are universally accepted as unquestionable." The possible isotopy of the elements—*vide infra*—has thrown a new light on this subject.

2. Why do so many groups of the elements exhibit family relationships?—If the elements are totally distinct and independent of one another, it is exceedingly difficult to reconcile the regularities and analogies of the elements in different groups revealed by a study of the triad families, and of Mendeléeff's law, the main characteristic of which is *relationship*. In the triads of the halogen family, said M. Faraday,[3] "we seem to have the dawning of a new light indicating the mutual convertibility of certain groups of elements, although under conditions which as yet are hidden from our scrutiny." These triads and the periodic law dimly foreshadow an identical origin or common parentage of families of elements. The possible isomerism of the chemical elements was discussed by J. F. W. Johnston, S. Brown, R. J. Kane, G. Wilson, etc. A study of the alkali metals, the metals of the alkaline earths, the halogens, etc., makes it highly probable that the different elements of one family, at least, have been formed by the conglomeration of monads or atomicules formed of the same primal matter so

as to build up ordinary atoms of different sizes or shapes, that is to say, evolution has progressed from homogeneity to heterogeneity. In other words, said C. R. A. Wright, the so-called elements are allotropic modifications of a primitive matter, and they differ from one another in the amount of latent energy they contain per unit mass. The idea is illustrated by the homologous series of carbon compounds. For instance,

	Ethene. C_2H_4	Propene. C_3H_6	Butene. C_4H_8	Pentene. C_5H_{10}	Hexene. C_6H_{12}
Mol. wt.	28	42	56	70	84

apparently by the polymerization of an increasing number of CH_2 groups. This series rises in a similar manner to nearly $C_{30}H_{60}$, with a regular increase of 14 in the mol. wt. J. W. Döbereiner's triads too have emphasized similar "constant" differences in the at. wt. of related elements. Hence, argued T. Carnelley, if a body we know to be compound can play the part of an element, there is some plausibility in the suggestion that the elements themselves are not absolutely simple.

3. Why are closely related elements so often associated together in nature?—Chemists have long been struck with the peculiar way certain elements occur in the half-mile crust of the earth. Although no disturbing agent has been recognized at work in nature whereby the different kinds of elements are sorted like to like, yet certain groups of elements nearly always occur in juxtaposition. These individual elements are not plentifully distributed, and they are not easy to separate from one another—*pares cum paribus facillime congregantur*. For example, cobalt is perhaps never quite free from nickel, and *vice versâ*; silver is almost invariably associated with lead ores and with gold; cadmium with zinc ores; selenium with the sulphur of pyrites; the members of the two groups of the platinum elements; the rare earths; etc. These associations and co-mixings cannot be entirely due to chance, for these elements are neither plentifully distributed nor have they any marked chemical affinity for one another. Consequently, it has been suggested that the elements in question were formed from some common material under almost identical conditions, and where slight variations in the conditions led to the almost simultaneous formation of closely related elements. Environment has determined the path of the evolution of the elements.

Additional circumstantial evidence for the unitary theory has been obtained from (4) the grouping of the spectral lines; (5) the magnetic and electric perturbations of the spectral lines; (6) the phosphorescent spectra of the rare earths; (7) spectra of the stars and nebulæ; (8) electric discharges in attenuated gases; (9) radioactivity; etc.

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§ 2. Spectrum Analysis

If there ever was a flank movement on Nature by which she has been compelled to surrender a part of her secrets, it was the discovery of the spectroscope, which enables us to peer into the very heart of Nature.—R. C. KEDZIE.

Near the beginning of the seventeenth century J. Kepler [1] mentioned the play of colours which occurs when a beam of sunlight is observed through a glass prism; and nearly half a century later, Isaac Newton proved experimentally that a beam of sunlight is composed of light rays of various colours perfectly blended and ranging from red through orange, yellow, green, and blue to violet. This Newton did by passing the beam of sunlight through a glass prism, and projecting the beam on to a screen. The violet, green, and blue rays are more bent in passing through the prism than the yellow, orange, and red rays. The beam of light after passing through the prism appears on the screen as an unbroken band of colours, which is called a **continuous spectrum.** Isaac Newton's work has been discussed by R. A. Houstoun. Any beam of white light can be used in place of sunlight, for instance, the light from an incandescent solid such as the limelight, Welsbach's mantle, incandescent carbon, etc. Isaac Newton admitted the beam of light through a circular aperture, but W. H. Wollaston, admitting the light through a narrow slit, noticed that the beam of sunlight furnished a spectrum which is crossed by a large number of **dark lines**—some sharp and well defined, others more or less faint and nebulous. J. von Fraunhofer happened to look at W. H. Wollaston's spectrum of the sun through a small telescope, and saw "an infinite number of vertical lines, darker than the rest of the spectrum, and some of them appeared entirely black." He carefully mapped the relative position of some 576 of these dark lines, and accordingly they are now generally called **Fraunhofer's lines.**

It was soon found that incandescent vapours and gases furnish a **discontinuous or line spectrum,** that is, a spectrum composed of a few **bright lines** instead of a continuous band. The line spectra of some elements are comparatively simple, for they display but a few clear distinct coloured lines—*e.g.* sodium a yellow line; thallium a green line; indium a blue and an indigo-blue line. Other elements have complex spectra containing numerous lines of varying intensity—*e.g.* barium, strontium, iron. The spectra of some elements, though complex, are easily recognized by the prominence and position of certain lines—*e.g.* the dark red line of rubidium, the blue line of cæsium, etc. The cause of the dark lines was quite inexplicable. As E. L. Larkin expressed it, "the human mind was now groping in darkness in the presence of one of the chief mysteries of nature." J. von Fraunhofer died without knowing their cause.

In 1822, D. Brewster interposed coloured glasses between the source of light and the slit, and found that the entire spectrum disappeared except the rays having the same colour as the glass; J. F. W. Herschel did the same with coloured liquids. In both cases, all waves of light were quenched except those transmitted by the medium. It was also found that the luminous lines in certain flames corresponded with the dark lines in the solar spectrum, and D. Brewster tried to use the spectrum in the analysis of simple and compound bodies. W. H. F. Talbot also said:

The orange ray may be the effect of strontian, as J. F. W. Herschel has found a ray of this colour in the flame of muriate of strontian. Were this opinion correct, a glance at the prismatic spectrum of a flame would be sufficient to show that it contained certain substances which could otherwise be discovered only by laborious chemical analysis.

It was provisionally assumed that J. von Fraunhofer's lines were due to the lack of certain shades of colour in the spectrum of sunlight. This plausible hypothesis was tested by L. Foucault in 1849. He arranged an experiment in which a ray of sunlight was directed by means of lenses on to the glowing gases between the poles of an arc light which alone gave a spectrum with two yellow lines very

prominent. The mixed light was passed through a prism. L. Foucault expected the lacuna in the solar spectrum corresponding with the yellow lines of the glowing gases in the arc light would be filled by the latter ; and that the yellow portion of the solar spectrum would be continuous. To his astonishment, the dark lines of the solar spectrum corresponding with the yellow lines were more pronounced than before. Hence the preliminary hypothesis cannot be true. L. Foucault then suggested the hypothesis that " the incandescent gases in the arc light have the power of absorbing the yellow from sunlight, as well as of emitting yellow light. The increase in the darkness of these lines is due to this absorbing power being greater than the emissive power." L. Foucault focussed the light from an incandescent carbon—which by itself gives a continuous spectrum—on to the incandescent gases between the carbon poles. Instead of getting the continuous spectrum of the incandescent carbon with yellow lines enhanced by the spectrum of the gases between the carbon poles, L. Foucault obtained a spectrum with the dark lines in the yellow portion. This experiment supported his hypothesis, **the same kind of light which a gas gives out when heated will be arrested if the attempt be made to pass the light through the gas ;** had L. Foucault known that the yellow lines were due to sodium he would have recognized the origin of Fraunhofer's lines. This interpretation was made by G. G. Stokes, 1852. In 1859, G. Kirchhoff definitely settled the question. He said :

> I formed a solar spectrum by projection, and allowed the solar rays concerned, before they fell on the slit, to pass through a powerful salted flame. If the sunlight were sufficiently reduced, there appeared in the place of the two dark lines, *D*, two bright lines ; if, on the other hand, its intensity surpassed a certain limit, the two dark lines, *D*, showed themselves in much greater distinctness than without the employment of the salted flame.

This discovery, said E. L. Larkin, is equal in importance to that of the law of gravitation, for the one may be said to weigh the universe, and the other to tell of what it is made. The subsequent history of spectrum analysis is but an illustration of the fact that when the right explanation of a phenomenon has been found, the facts seem to arrange themselves about the theory as naturally as the particles of a salt in a soln. aggregate about the enlarging nucleus of a crystal.

R. Bunsen and G. Kirchhoff subsequently proved that, under like conditions of temp. and press., **every element in the gaseous state has its own characteristic spectrum ; and reciprocally, the presence of the vapour of an element can be inferred with certainty when the characteristic lines are present.** The spectrum of an element is so definite and characteristic that it has been proposed to use this fact as part of the definition of an element. The spectrum of an incandescent vapour of a mixture of elements contains all the lines characteristic of each element in the mixture, and consequently it is possible to recognize each and all of them by measuring the position of the bright lines and comparing the lines with those of known elements. This method of detecting elements is called **spectrum analysis.** R. Bunsen and G. Kirchhoff were able to prove that the dark Fraunhofer's lines are due to the rays of light from an incandescent solid passing through vapours of various elements. For the characteristic bright lines of, say, sodium are changed into dark lines when the white light from an incandescent solid is allowed to pass through the vapour of this element. Hence, since the bright lines of the spectrum of a vapour are changed into dark lines, and the dark parts of the spectrum are changed into bright colours by the continuous spectrum of white light, it seems as if the whole spectrum is reversed with respect to the illumination. Hence, G. Kirchhoff called it a **reversed spectrum.** It also follows that Fraunhofer's lines are due to the rays of light from an incandescent sun passing through the sun's atm., and consequently the vapours of the elements whose line spectra correspond with the dark lines of the solar spectrum must be present in the sun's atm., and consequently

> The spectrum catches tokens from his light
> Of elemental kinship with the earth.—C. A. Lane.

By the aid of spectrum analysis, therefore, it has been possible to deduce the presence of a large number of known elements—nearly 40—in the sun's atmosphere from the coincidence of the bright lines furnished by elements in the laboratory with the dark lines in the solar spectrum. The halogen elements, nitrogen, oxygen, gold, mercury, and a few other elements, have not been detected in the sun. The spectrum of an unknown element—helium—was observed in the solar spectrum some thirty years before the corresponding element was discovered in the earth. The light from the fixed stars furnishes results similar to those obtained with sunlight. The lines of hydrogen, helium, carbon, magnesium, calcium, and iron have been detected in nebulæ; and hydrogen and hydrocarbons have been recognized in comets.

The light from incandescent solids furnishes a continuous spectrum, but the spectra of gases and vapours are discontinuous and furnish line spectra. The spectrum of an element can be excited by feeding it into a flame—*flame spectrum;* by passing it through an electric arc—*arc spectrum*—or through the electric spark discharge—*spark spectrum;* by the action of light of suitable frequency—*fluorescent emission spectrum.* The *lines* of the characteristic spectrum of an element obtained under low dispersion are usually resolved into a number of *components* with a high dispersion. If some of the components of a line are very close to and faint compared with the others, they are called *satellites* of the brighter components. With a still higher dispersion, a stage is reached at which no further components of a line can be observed. The distinction, however, is largely one of degree. The wave-length of a complex line is that which would be obtained with a dispersion too small to resolve it into its components. In addition to one or more characteristic *line spectra*, some elements also show a **band spectrum.** Compounds usually emit continuous or band spectra, or else the line spectra of the constituent elements. In a typical band spectrum, there are a number of bands each consisting of a large number of lines ranged together in close sequence. The lines are more closely crowded at one end, which is regarded as the *head* of the band, while the crowding gradually becomes less towards the other end or *tail* of the band. J. Plücker and W. Hittorf, and J. Salet assumed that different allotropic forms are involved in the different spectra furnished by a gas. H. von Helmholtz suggested that the line spectra are produced by atoms, band spectra by molecules. This idea was developed by E. Wiedemann, A. J. Angström and R. Thalen, A. Wüllner, F. Zöllner, etc. In general, band spectra are characteristic of compounds, not elements; and the bands in the spectrum of nitrogen are assumed to be produced by the nitrogen molecule, not its atom.

Isaac Newton favoured the assumption that "light consists of exceedingly minute particles shot out from a luminous body, and causing the sensation of light when impinging on the retina." Newton's corpuscular theory explained the reflection and refraction of light very well, but it left unexplained numerous other phenomena. In 1678, C. Huygens suggested the wave theory of light, and his ideas were subsequently developed by T. Young and A. Fresnel. J. C. Maxwell showed that both light and electromagnetic phenomena are produced by waves transmitted through the æther, which differ only in their wave-length. A similar parallelism exists between ultra-violet light and the X-rays.

The theory of the spectrum is based on the hypothesis that every ray of light is propagated by a kind of vibratory, undulatory, or wave-motion, which possesses energy. The medium which propagates light is the immaterial plenum called the unknown æther. The æther is therefore an hypothesis to assist in picturing a mechanism by which energy can be propagated through space, and it is assumed that light is propagated by the vibratory or wave-motion of the æther. The velocity of light approximates 200,000 miles or 3×10^{10} cm. per sec., while the molecules of a gas travel about a quarter of a mile or $4{\cdot}5\times10^{4}$ cm. per sec. There are two ways of measuring wave-motion: (1) the *vibration frequency* represented by the number of vibrations per sec.; the vibration frequency may also refer to the number of vibrations per cm., and is usually symbolized by ν; and (ii) the *wave-length* represented

by the distance from crest to crest or trough to trough of a vibration, and usually symbolized by λ. The greater the frequency the shorter the wave-length and conversely. If V be the velocity of light, 3×10^{10} cm. per sec., the frequency representing the number of vibrations per cm. is represented by $\nu=V/\lambda$; but this unit, though used in theoretical work, is too large, and it is common to employ $\nu=1/\lambda$ in experimental work. The wave-length can be expressed in terms of μ, *i.e.* 0·001 mm., or $\mu\mu$, *i.e.* $0{\cdot}001\mu$ or 0·000001 mm., or in ten-millionths of a metre, 10^{-10} m., *i.e.* $0{\cdot}1\mu\mu$, the last are called Angström's units—symbolized A—*e.g.* $0{\cdot}589\mu=589\mu\mu=5890$ A. The spectral lines of the different elements are referred to a scale of wave-lengths, and usually expressed in Angström's units. J. von Fraunhofer designated the chief lines he noted in the solar spectrum by the letters *A*, *B*, *C*, *D*, . . ., and since some of these lines coincide with the characteristic lines of known elements, certain lines of certain elements are sometimes designated by Fraunhofer's letters —*e.g.* the *D*-line of sodium.

The differently coloured rays of light depend on differences in the rates of vibration, or vibration frequency. There is a specific rate of vibration for each colour. There are myriads of rays of different wave-length in a beam of white light. It is the function of the spectroscope to separate these waves, so that the different rays are sorted in the order of their vibration frequency or wave-length. In the spectrum, the rays which produce the sensation of red are slowest, the violet fastest. When the eye receives nearly 400 billion of these vibrations per sec., it is agreed that the colour sensation is red; and if nearly 750 billion per sec., violet. All the different colours of the spectrum lie between these extremes. Otherwise expressed, the eye recognizes as light only those vibrations of the æther ranging between a wave-length 81 millionths of a cm. at the red end and 36 millionths of a cm. at the violet end. Some people's eyes are tuned to see a little further than others into the ultra-violet or the ultra-red.

In 1800, J. F. W. Herschel discovered the existence of the so-called **ultra-red rays** or the invisible heat rays in the region beyond the red in the visible spectrum; and the following year, J. W. Ritter discovered the so-called **ultra-violet rays** in the region beyond the violet of the visible spectrum. Two hypotheses were then invented: One assumed that there are three distinct types of rays present in light—the heating, the visible, and the actinic. It was further supposed that these rays overlapped somewhat in refrangibility, and thus the heating rays appeared in the red and orange, and the actinic in the violet and blue. The other hypothesis supposed all the rays to be the same in nature, *viz.* undulations in the æther; but the ultra-red and ultra-violet rays were supposed to differ somewhat in quality or intensity which made them invisible. Thus, the undulatory theory is monistic. It was championed by J. B. Biot in 1814 and by A. M. Ampère in 1832. The wave-length of the rays at the violet end of the spectrum is 4×10^{-5} cm., and at the red end, $7{\cdot}5\times10^{-5}$. The wave-length of the ultra-red rays have been measured to 3×10^{5} cm.—these waves correspond with the æthereal vibrations of the electromagnetic waves used in wireless telegraphy; and J. Schumann measured the wave-length of ultra-violet rays to $1{\cdot}22\times10^{-5}$ cm., or 1200 A., *Schumann's waves*. T. Lyman down to $0{\cdot}51\times10^{-5}$, or 510 A., and R. A. Millikan and co-workers down to $0{\cdot}32\times10^{-5}$ cm., or 320 A. The X-rays have a wave-length between 10^{-8} and 10^{-9}. The visible spectrum thus represents a very limited region in the range of known æthereal vibrations, which progressively increase from 10^{-5} to 3×10^{5} cm., and differ only with regard to the detectors employed to determine their presence. The term light is therefore extended, and it does not necessarily mean only visible light.

The rays at the red end of the spectrum produce thermal effects, and the energy of these heat rays has been explored in different parts of the spectrum and extended into the ultra-red. The rays at the violet end of the spectrum are the most active chemically, and these actinic rays extend well into the ultra-violet. The light at the red end of the spectrum are the least active chemically. These facts are utilized by the photographer, who employs ruby-glass or red screens to

cover the windows and lamps used for the dark-room. The ultra-violet rays are largely absorbed by glass, though quartz is fairly transparent to these rays. In illustration of the chemical activity of these rays, they decompose silver salts; the iodides of potassium, sodium, calcium, barium, zinc, etc.; ferric sulphate, nitrate, or chloride is reduced to the ferrous salt particularly in the presence of organic matter—*e.g.* cane sugar; soln. of chlorates and bromates are quite stable if exposed to sunlight in glass bottles, but they are appreciably reduced by light if kept in quartz vessels. The rate of reduction is augmented if sugar is present. Ultra-violet light decomposes ammonia, nitric and nitrous oxides, and carbon dioxide; it induces the combination of oxygen with hydrogen or carbon monoxide; and produces with oxygen, ozone; ultra-violet light ionizes air and other gases, and it produces the so-called photoelectric effect.

It might be added that the spectrum of a gas depends partly on the *temperature* and partly on the *pressure* under which the gas is confined. In passing to a higher temp., new lines are often added to a spectrum, and old lines disappear; for instance, the lithium spectrum in the electric arc shows a blue line not visible in the spectrum obtained by Bunsen's flame. The character of the lines also depends upon the temp. under which the gas or vapour is examined. Sodium in a Bunsen's flame, for instance, gives one well-defined yellow line which is really compounded of two yellow lines; but at higher temp. three other pairs of lines make their appearance. The difference between the high and low temp. spectra is sometimes so marked that in the early days of spectroscopy J. Plücker and W. Hittorf wrote: "There is a certain number of elementary substances which when differently treated furnishes two kinds of spectra of quite different character, not having any line or band in common." The variations in the spectra are characteristic, and *it is possible to deduce the approximate temperature from the corresponding spectrum of a substance.* In a general way, it may be said that the spectra of elements become more complex as the temp. is raised. In the case of compounds, too, A. Mitscherlich showed that they may have a characteristic spectrum in which no lines of the constituent elements can be detected; but if the temp. be high enough to decompose the compound, the characteristic lines of the constituent elements will appear. The spectra of some elements are influenced by the *medium*, so much so that the spectra may be obliterated or suppressed. The subject has been studied by G. E. Gibson and A. A. Noyes, etc.

At small pressures, spectra with broad bands are obtained. As the press. is increased, "new series of lines arise which existed only in germ at lower pressures"; the bands give way to lines, and finally a continuous band of light is obtained corresponding with the pure spectrum. Under great press., all incandescent solids, liquids, and gases emit continuous spectra. A. Wüllner, A. Schuster, G. Ciamician, G. D. Liveing and J. Dewar, etc., studied the widening of the spectral lines by press. E. Frankland and J. N. Lockyer found that if the press. of hydrogen be increased while an electric current is passing through the gas, the lines begin to expand until the spectrum becomes continuous, and finally, the resistance becomes so great that a current will not pass. J. P. Gassiot, and J. Plücker also found that if the press. of hydrogen be diminished, the electrical resistance attains a minimum; then increases, and finally becomes so great that a current will not pass. Hence, added A. Schuster, the resistance of the gas may be assumed to be the same when the current just ceases to pass, whether the increased resistance is produced by too great or too low a press. In the former case the gas is not heated so much as in the latter case, and yet the spectrum is not continuous nor are the lines widened. Hence, the observed widening of the lines, observed by E. Frankland and J. N. Lockyer, is not caused by a rise of temp. but by press. The widening in the spectra of some substances begins with the more refrangible lines, and in that of others, with the less refrangible lines. Thus, J. Plücker and W. Hittorf found the widening with hydrogen begins with the more refrangible lines; G. Ciamician found mercury behaved similarly. With oxygen, J. Plücker and W. Hittorf found the widening begins with the less refrangible

lines, and with sodium, and rubidium, J. N. Lockyer observed similar results. J. N. Lockyer found the 4210-silver line widened on the more refrangible side, and the 4054·3-silver line on the less refrangible side. T. R. Merton has discussed the subject. J. S. Ames, W. J. Humphreys and J. F. Mohler found that the press. does not act in the same way on the rays of different series of spectral lines, but for a given series they represent the effect of a change of press., dp, on the wave-length, λ, by $d\lambda=\lambda\beta.dp$, where β is constant for a given series. R. S. Hutton and J. E. Petavel studied the effect of press. up to 100 atm. on arc spectra.

Some substances absorb certain colours and transmit others; they may absorb light in lines as narrow and sharp as the lines in the emission spectrum. They were observed in the case of sodium vapour whose absorption spectrum appears as a dark line in the continuous background. The lines in the absorption and continuous spectra are not necessarily the same. Hydrogen, for instance, under normal conditions does not absorb any of the characteristic lines of its emission spectrum. If a coloured soln. be illuminated by the light from an incandescent solid transmitted through the soln., a series of dark bands or lines, called the absorption spectrum, is obtained. A number of soln. have very characteristic absorption spectra—*e.g.* blood, didymium chloride, copper sulphate, potassium chromate, potassium permanganate, potassium dichromate, etc. H. C. Jones and co-workers measured the absorption spectra of a number of soln., and inferred that the solute forms compounds with the solvent. They say that there is a gradual shift in the absorption band as one salt is transformed into another by the replacement of the acid radicle owing to the formation of intermediate compounds. T. R. Merton, however, showed that this statement is a mal-inference, and is readily explained by the superposition of two absorption curves; he also observed that press. up to 750 atm. had no influence on the absorption spectra of soln.

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§ 3. Evidence for the Unitary Theory from Spectrum Analysis

The final impression our mind receives on contemplating these fundamental relations is that of a wonderful mechanism of nature, the functions of which are performed with never-failing certainty, though the mind can only follow them with difficulty, and with a humiliating sense of the incompleteness of its perception.—J. J. Balmer.

To produce light something must vibrate. It is assumed that the seat of the impulses which set up wave-motion in the æther are vibrating molecules, atoms, or maybe sub-atoms. It is assumed that each particular band or line is an effect of the periodic vibrations of particles, and that the line spectra are produced by vibrations confined to atoms, or parts of atoms, while with band spectra the vibrations are similarly confined to the molecules. Owing to the fact that each gas, when heated, has its own characteristic spectrum, it is inferred (i) that the rates of vibration of the particles of the hot gas which give rise to the spectrum are constant and characteristic ; and (ii) that the vibrating particles of the gas set up corresponding vibrations in the æther which are recognized as light rays with a specific spectrum. The fact that the same kind of light emitted by a hot gas is arrested when the attempt is made to send that light through the gas, is taken to mean that when the rate of vibration of any ray of light coincides with the rate of vibration of the particles of the gas, the light will be more or less completely quenched by those particles because the energy of the light ray will be expended in setting those particles into vibration. W. C. D. and C. D. Whetham [1] express the idea of sympathetic vibrations neatly :

A child's swing is set in motion by giving it a series of small impulses which coincide with its natural period of oscillation, and in a similar manner any mechanical system will absorb energy which falls on it in rhythmic unison with its own natural vibrations.

Conversely, if a gas be heated sufficiently to set the particles vibrating vigorously enough to give out light, then the light will have the same colour as that which the gas could stop. The particles will act as storm centres and send out waves into the æther which appear as light. The absorption of different coloured rays by different gases thus indicate that the particles of a gas possess specific rates of vibration. The compression of a gas does not effect the rates of vibration of the particles or of the colours absorbed by the gas because the same coloured rays are absorbed by the compressed gas as were absorbed by the gas under ordinary press. Hence, the vibration is not a property of the gas as a whole—for the properties of a mass of gas are altered by compression—but it is a property of the separate parts of a gas which are only brought closer by compression while their rates of vibration are not affected. G. Ribaud studied the kinetic theory of the absorption of energy by the molecules of a gas.

The constancy of the spectral lines in the spectrum of a gas shows that the motions of the vibrating particles must be remarkably regular. The period of vibration of the particles, as revealed by the spectroscope, conditions a chemical property which, in the opinion of R. Bunsen, is as constant and fundamental as the at. wt. of the element, and which may be determined with very great exactitude ; indeed, in 1900, the International Congress in Paris accepted a proposal by A. de Gramont that **no new substance be recognized as an element until its spark spectrum has been measured, and shown to be different from that of every other known form of matter.** The large number of spectral lines in the spectra of many elements, *e.g.* iron, shows that the vibrations which give rise to the spectrum must be remarkably complex. According to J. N. Lockyer, the lines are connected with the different vibratory powers of different portions of an atom. In other words, an atom is a

complex aggregate of particles, and hence H. A. Rowland was led to say that a grand piano must be a simple mechanism in comparison with a vibrating atom. All this is supposed to imply that the spectral lines are due to the vibrations of particles smaller than the atom, and that **the atom itself is a complex system made up of vibrating corpuscles.** Indeed, *the atom itself is now considered to be a kind of miniature planetary system embracing numbers of corpuscles each spinning in its own tiny orbit.* This recalls the speculation, where the individual atoms were supposed to whirl rhythmically in minute orbits to form molecules, much as the planets in the solar system revolve about the sun. The idea is quite an old one. S. Brown, for example, in 1843, said :

> The atom is by no means essentially or even potentially indivisible. There is a possibility and likelihood that within the atom is another nameless world of the universe. Under the sky of the atom proceed worlds of material existence as different from atoms as atoms from compound particles ; as compound particles from crystal shapes ; as crystal shapes from stars and planets ; as stars and planets from solar systems ; or as solar systems from firmaments.

It will be observed that at least three characteristic spectra of an element may be possible, for the spectrum may be produced by the oscillations (i) of the molecule as one unit ; (ii) by the atom as one unit ; and (iii) by the sub-atoms, or parts of the atom. The recognition of the fact that the spectrum of an element depends on the structure of its molecules or atoms, induced hopes that a study of spectra would teach something about the structure of matter. The problem appeared to be immensely complex. Thus, R. W. Wood said :

> The study of the structure of the molecule by means of the spectroscope might be likened to the attempt on the part of an individual who had no experience with or conception of any musical instrument to get a clear idea of all the musical instruments of an orchestra by listening to a concert.

The acoustical analogy encouraged investigators to seek for simple harmonic relations between the frequencies of the molecular vibrations, such as the whole-number ratios known to exist between the fundamental note and the overtones of an organ-pipe or piano-string. Thus, E. Mascart, L. de Boisbaudran, J. L. Soret, G. J. Stoney, G. D. Liveing and J. Dewar joined in the quest. At first glance, the spectral lines of a given element seem to be so complex that any attempt to reduce them to order appears to be hopeless. According to F. Exner and E. Haschek, the arc spectrum of uranium contains 4940 lines, and the spark spectrum 5655 lines. H. Kayser and C. Runge tabulated 4500 lines in the spectrum of iron. As a rule, the spectra of elements with large at. wt. are more complex than those of elements with low at. wt. G. J. Stoney noticed a semblance of order in the spectrum of hydrogen ; and A. Schuster asked : Is the number of whole-number ratios between the wave-lengths greater than would exist if the lines were distributed at random ? After examining the spectra of sodium, copper, barium, magnesium, and particularly iron, he concluded that the whole-number ratios were less than would be expected on a chance distribution. J. J. Balmer found that the wave-lengths of most of the hydrogen lines can be computed if whole numbers be substituted for m in a formula of the type $3647{\cdot}2m^2/(m^2-4)$, *vide* hydrogen, **1.** 7, 7. The numerical relations between the lines of a spectrum are more readily discerned when the frequencies, ν, are substituted for the wave-lengths, λ, as indicated above, where $\nu=\lambda^{-1}$. In the search for analogous laws in the spectra of other elements, it was found that the lines of many apparently chaotic spectra can be resolved into a number of regular series superposed one on the other. Thus, **the spectral lines of the elements can be arranged in groups or series.** The spectrum of helium, for example, can be resolved into eight such series, each of which has lines which show a regular decrease in intensity with vibration frequency. Oxygen has a spectrum with six superposed sets of lines ; hydrogen and the alkali metals have each four such series. The metals in question have monatomic molecules, and hence it inevitably follows that the atoms

have a complex constitution, and that **the spectral lines are not all produced by the vibrations of the same kind of particles ; atoms are complex aggregates of vibration corpuscles.**

L. de Boisbaudran emphasized the similarities in the spectra of related elements. Some of these relations have been applied to estimate the at. wt. of the elements—*vide* gallium, and radium. He said :

> In the natural families of elements, the variation in the increment of the at. wt. is proportional to the variation in the increment of the wave-length of homologous rays or groups of rays in the third harmonic of the spectrum.

Although the spectrum of each element is characteristic of that element and of no other, yet the spectrum of each of the five alkali metals can be resolved into four homologous series such that every line in one spectrum is represented by a corresponding line on all the other spectra ; and generally, **the spectra of related elements form natural or homologous groups.** The corresponding lines do not necessarily all occur in the visible spectra, *e.g.* the dark red line of the rubidium spectrum corresponds with a line in the ultra-red in the other spectra ; and the yellow lines of the sodium spectrum are homologous with lines in the ultra-violet spectra of the other elements. The spectra of related elements seem to be subject to a law of homology which is closely connected with their at. wt. Each series of homologous lines appears to contract in passing from one element to another so that as the at. wt. increases, the lines at the red end of the spectrum appear to open further apart, and at the violet end, to draw closer together. Thus, C. Runge represented the spectral lines of the alkali metals by dots, Fig. 1, so that their limits at the violet end coincide ; it will be seen that the lines of this particular series contract in passing from lithium to cæsium, and the relation between the contractions and the at. wt. of the elements is shown in the diagram by making the distances between the lines represent the magnitude of their at. wt.—*vide* **2**. 20, 7. Similar remarks apply to the spectra of many other families of elements.

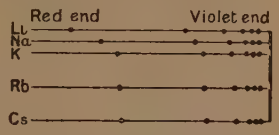

FIG. 1.—One Series of Homologous Spectra of the Alkali Metals Spaced according to their Atomic Weight.

According to D. I. Mendeléeff, the chemical and physical properties with the odd or even series of elements in the periodic table, resemble one another more closely than they do with elements immediately adjoining. Thus, the spectra of gallium, indium, and thallium in the third odd series resemble more the spectra of their homologous potassium, rubidium, and cæsium in the first series, than the spectra of their homologous calcium, strontium, and barium in the second even series. In a given natural group, C. Runge found that with increasing at. wt. in chemically related series, *i.e.* the vertical series of the periodic table, the spectral lines shift towards the less refrangible or red end ; while the spectra of elements in a horizontal series—*e.g.* like sodium and magnesium, potassium and calcium, etc.—shift in the opposite direction, so that the spectrum of an element with the greater at. wt. is as a whole situated nearer the more refrangible or violet end. The difference, ν, in the vibration frequency of a doublet in the spectra of the elements in a given family is proportional to the squares of the at. wt., A, and the values of νA^{-2} lie on a straight line, as illustrated by Fig. 2. The values of lithium, sodium, and aluminium deviate from the straight line belonging to the members of their respective families. Many of the relations between the properties of the elements and the at. wt. also apply to the at. numbers.

There is thus a family likeness between the spectra of related elements, and a close connection has been traced between the at. wt. and the differences in the vibration frequencies of the lines in the members of a given family of elements. The at. wt. of groups of related elements with their related physical and chemical properties differ by definite values, and the spectra of these elements show that

the masses of their atoms affect their rates of vibration in a similar manner. This is taken to mean that **not only is an atom of an element a complex composed of different aggregates of particles, but the atoms of allied elements are built up of similar aggregates of particles;** and the observed differences in the spectra of allied elements results from differences in the way these aggregates are arranged in the atom. The assumption that light is produced in the atom by the oscillations of electrons about a positive nucleus is discussed in connection with the structure of the atom, and the mathematical treatment has been very successful in explaining the line spectra.

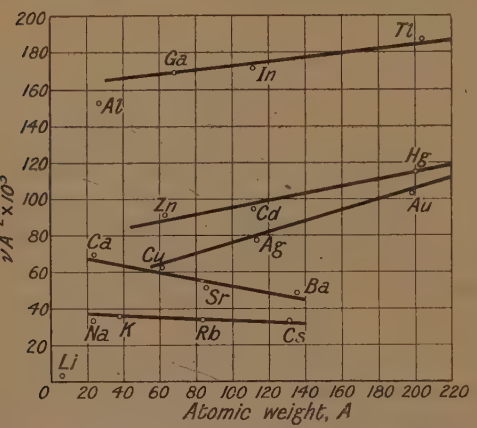

FIG. 2.—Relation between Vibration Frequency and Atomic Weights of the Elements.

In general, the line spectra which have been reduced to order, show that the frequencies of the lines in a spectrum follow a definite law; and that law is always of the same type. Such spectra are called series spectra—*e.g.* the series spectra of the alkalies, alkaline earths, and many metals. The spectra of the elements on the left of the periodic table appear simpler than those on the right, and the series spectra of the latter have not yet been resolved. W. Ritz showed that (i) when the frequency of every line can be represented as the difference between the frequencies of two other lines in the spectrum; and (ii) it is possible to find pairs of lines with the same frequency difference, then usually the spectrum lines can be resolved into terms of a series although it may not be possible to complete the analysis. W. Ritz called this **the principle of combination**—*das Kombinationprinzip.*

The formula of J. J. Balmer

$$\lambda = b\frac{m^2}{m^2-n^2}; \text{ or } \nu = A - \frac{n^2 a}{m^2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A, a, and b are constants, and m and n are integers, gave excellent results for hydrogen when $n=2$. H. Kayser and C. Runge series formula (1888) is

$$\nu = A + Bm^{-2} + Cm^{-4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A, B, and C are constants, and m is integral; analogous formulæ with three terms with the powers m^{-1} and m^{-3} were also suggested. This formula is to be regarded as the ordinary series formula commonly employed when the form of a function is unknown. J. R. Rydberg's series formula (1889) is

$$\nu = A + \frac{N}{(m+a)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where m is any integer; and a is a number between unity and zero; A is a constant; and N is a universal constant. J. R. Rydberg's formula is sometimes written $\nu=(m, a)$. H. Ramage (1900) used a slight modification of J. R. Rydberg's formula. L. Rummel (1896) employed $\lambda = a + b/(m^2-c)$, where a, b, and c are constants, and m is an integer; A. Fowler and H. Shaw (1903) used $\nu = \nu_0 - N/\{(m+\mu)^2 - m_0\}$, where μ, ν_0, and m_0 are constants; and also $\nu = \nu_0 - N/(mp - m_0)$, where p is a constant. In W. Ritz's series formula (1903), $\nu = N(p^{-2} - q^{-2})$, where $p^{-2} = m + a + \beta m^{-2} + \gamma m^{-4} + \ldots$; $q^{-2} = m + a' + \beta' n^{-2} + \gamma' n^{-4} + \ldots$. By omitting the higher members of the series, this assumes the form of

$$\nu = A - \frac{N}{(m+p_i+\pi_i m^{-2})^2}; \text{ or } \nu = A - \frac{N}{\{m+p_i+\pi_i(A-\nu)\}^2} \quad . \quad . \quad (4)$$

where N is the universal constant, and p_i and π_i are numbers which have rather different values. These expressions are related to J. R. Rydberg's formula. W. Ritz used the first, and F. Paschen the second, of formulæ (4). J. Halm (1904) employed $(\nu_\infty - \nu)^{-1} = a(m+\mu)^2 + b$, where ν_∞, a, μ, and b are constants. T. van Lohuizen (1912) employed a complex expression

which can be simplified until it resembles the second of formulæ (4). E. E. Mogendorff (1905) and W. M. Hicks (1910) used the formula

$$\nu = A - \frac{N}{(m+a+bm^{-1})^2}$$

where A, a, and b are constants. Assuming that $\nu=(m, a)$ represents equation (3), a typical spectrum in which there are four groups of series with $a=s, p, d$, and b, where m in the s-group may have any value from unity upwards; in the p-group, any value from 2 upwards; in the d-group, any value from 3 upwards; and in the b-group any value from 4 upwards. Then, the different series of lines are:

PRINCIPAL SERIES.		SUBSIDIARY SERIES.	
First	$\nu=(1, s)-(m, p)$;	First or diffuse	$\nu=(2, p)-(m, d)$
Diffuse	$\nu=(1, s)-(m, d)$;	Second or sharp	$\nu=(2, p)-(m, s)$
Sharp	$\nu=(1, s)-(m, s)$;	Third	$\nu=(2, p)-(m, p)$
	Bergmann's series		$\nu=(3, d)-(m, b)$

where the m in the second term is greater by one than the constant number in the first. The principal series always contains the most intense characteristic lines of the elements. F. A. Saunders, A. del Campo and M. A. Catalan, A. Kratzer, O. Oldenberg, P. D. Foote and F. H. Mohler, and A. Fowler have also discussed series spectra.

When a solid is heated to a high enough temp., light is emitted; and this light can be resolved into a continuous spectrum. The distribution of the energy for light of different wave-lengths can be measured by a bolometer. In general, the relation between the intensity of the radiant energy and the wave-length depends on the nature and temp. of the heated body. A uniformly heated enclosure, which absorbs completely all the radiation falling upon it, is a perfect radiator of heat; and the thermal radiation which it emits is a function of temp. only, and is independent of the nature of the material. A substance possessing such properties is called a *black body*. No known substance is a perfect black body—lamp-black is a close approximation; platinum and white oxides depart considerably from black-body radiation. The relation between the temp. T, and the energy of black-body radiation, E, established by J. Stefan, L. Boltzmann,[2] and O. Lummer and E. Pringsheim, is $E=5{\cdot}6\times10^{-5}(T^4-T_0^4)$ ergs per sq. cm. per sec. This is known as the **Stefan-Boltzmann radiation law.** Here T denotes the absolute temp. of the radiating body, and T_0 the temp. of the body receiving the radiations.

Lord Rayleigh found the relation between the radiant energy, E; the wave-length, λ, or the vibration frequency, ν; and the absolute temp., T, is

$$E=\frac{VkT}{\lambda^4}; \quad E=\frac{\nu^2}{V^2}kT$$

where V denotes the velocity of light, 3×10^{10} cm. per sec.; and k is the so-called gas constant per atom or $1{\cdot}37\times10^{-16}$ ergs per degree. W. Wien gave

$$E=V^2h\lambda^{-5}e^{-\frac{Vh}{kT}}; \quad E=h\nu^3V^{-2}e^{-\frac{h\nu}{kT}}$$

where h is the universal gas constant, $6{\cdot}62\times10^{-27}$ erg-sec. M. Planck gave

$$E=\frac{V^2h\lambda^{-5}}{e^{\frac{Vh}{k\lambda T}}-1}; \quad E=\frac{h\nu^3V^{-2}}{e^{\frac{h\nu}{kT}}-1}$$

W. Wien's equation fits low values of λT; Lord Rayleigh's high values; and M. Planck's is applicable over the whole range.

M. Planck's radiation formula is alone based on the quantum theory of energy—**2.** 13, 15. The formulæ of Lord Rayleigh, and W. Wien are based on electrodynamics, and thermodynamics and the equipartition of energy—**2.** 13, 10. M. Planck assumes (i) that there exists in the enclosure linear oscillators similar to those used in the production of Hertzian waves but of molecular dimensions, so that the frequencies of the harmonic vibrations emitted by them are of the order of magnitude of those present in the radiation from the black body; (ii) that an oscillator cannot take up energy continuously, but *discontinuously in multiples of a unit*

quantum ϵ; and (iii) that the unit quantum which the oscillator can emit or absorb is proportional to its frequency, ν; that is, $\epsilon=h\nu$, where h is a universal constant. He added:

> In what way we are to conceive the nature of quanta of a purely dynamical nature, we cannot yet say for certain. Possibly such quanta might be accounted for if each source of radiation can emit energy only when that energy attains at least a certain minimum value; just as a rubber pipe, into which air is gradually compressed, bursts and scatters its contents only when the elastic energy in it attains a certain value. In any case, the hypothesis of quanta has led to the idea that there are changes in nature which do not occur continuously but in an explosive manner. I need hardly remind you that this view has become much more conceivable since the discovery and investigation of radioactive phenomena. Besides, all difficulties connected with detailed explanation are at present overshadowed by the circumstance that the quantum hypothesis has yielded results which are in closer agreement with radiation-measurements than are all previous theories.

According to the quantum theory of energy (**1.** 13, 15), if h is the universal constant or $6{\cdot}62\times10^{-27}$ in erg-sec. units; ν the vibration frequency of the radiation; and W the radiant energy; then $W=h\nu$, or $nW=nh\nu$, where n is an integer usually unity. This expression means that radiant energy of frequency ν is always radiated in bundles or quanta. The yellow sodium D-line has a wave-length $0{\cdot}5896\mu$, so that the vibration frequency is $\nu=3\times10^{10}\div0{\cdot}5896\times10^{-4}=5{\cdot}088\times10^{14}$; and $h\nu=6{\cdot}62\times10^{-27}\times5{\cdot}088\times10^{14}=33{\cdot}69\times10^{-13}$ ergs. Hence, remembering that a watt is 10^7 ergs per sec., it follows that the energy quanta involved are very small. If the conservation of energy is applicable, then in passing from a state a to a state b, the atom parts with energy W_a-W_b. It is shown that atoms may occur in (i) a normal or electrically neutral state, and (ii) the charged or ionized condition. If each of these states has a characteristic spectra, and all other states are intermediate between these two, then the work required to make the atom pass from the state a to the state b is equal to the work of ionizing the atom. The terms of the spectrum of an element converge to zero frequency at one end, and cease at a frequency ν_a at the other end, the extreme difference of frequency is ν_a, so that the extreme difference of energy should be $h\nu_a$, and this should represent the work, W_0, required to ionize the atom, or $W_0=h\nu_a$. The **ionizing potentials** of some metal vapours are shown in Table I, and the results are well in accord with the hypothesis. h is here expressed with the volt as unit of energy and 3×10^{-10} sec. as the unit of time. To express h in ergs multiply the tabulated values by $5{\cdot}30\times10^{-23}$. This

Table I.—Ionizing Potentials of Vapours.

	Ionizing potential W_0 volts.	Frequency ν_a per cm.	Ratio $W_0/\nu_a=h$.
Mercury	10·38	$6{\cdot}17\times10^4$	$1{\cdot}257\times10^{-4}$
Cadmium	8·9	$7{\cdot}25\times10^4$	$1{\cdot}23\times10^{-4}$
Zinc	9·5	$7{\cdot}58\times10^4$	$1{\cdot}25\times10^{-4}$
Cæsium	3·9	$3{\cdot}14\times10^4$	$1{\cdot}24\times10^{-4}$
Rubidium	4·1	$3{\cdot}37\times10^4$	$1{\cdot}22\times10^{-4}$
Potassium	4·1	$3{\cdot}50\times10^4$	$1{\cdot}17\times10^{-4}$
Sodium	5·13	$4{\cdot}14\times10^4$	$1{\cdot}238\times10^{-4}$

gives a mean value $6{\cdot}52\times10^{-27}$. J. H. Jeans, C. F. Bickerdike, etc., have discussed the relation between radiation and the emission of electrons; K. T. Compton has discussed the ionization of gases at potentials below the so-called ionization potential. The subject is discussed in A. Sommerfeld's *Atombau und Spektrallinen* (Braunschweig, 1919); in N. R. Campbell's *Series Spectra* (Cambridge, 1921); in A. Fowler's *Report on Series in Line Spectra* (London, 1922); in W. M. Hicks' *A Treatise on the Analysis of Spectra* (Cambridge, 1922); and P. D. Foote and L. F. Mohler's *The Origin of Spectra* (New York, 1922).

Band spectra are assumed to be produced by molecules, spark spectra by ionized atoms, and arc and flame spectra by neutral atoms. Hence, W. Kossel [3] and A. Sommerfeld infer that the spark spectrum of an element corresponds with the arc spectrum of the preceding element in the periodic table. This has been discussed by E. Fuess, A. Sommerfeld, and W. Reis. There have been a number of attempts—by R. Thalen, L. de Boisbaudran, G. J. Stoney, G. Salet, A. S. Herschel, and T. N. Thiele—to find relations in the band spectra of the elements and compounds. H. Deslandres gave for the frequencies of the lines making up a single band

$$\nu = A + Bm^2$$

where m is a successive series of integers ; and A and B are constant, A representing the head of the band when $m=0$. The formula was tested by H. Kayser and C. Runge, but it does not accurately represent the facts—particularly for small values of m. Other formulæ have been proposed by G. Higgs, G. Halm, C. Fabry, and P. Weiss. A theoretical foundation for the formula was laid by N. Bjerrum on the assumption that (i) band spectra are produced by the rotational energy of rigid polyatomic molecules ; and (ii) the emission and absorption of radiant energy in band spectra represent changes in the rotational energy which occur in accord with the quantum theory.

In equation (7) (3. 27, 3), it is shown that the kinetic energy, W, of a rigid molecule of mass m, rotating in a circular orbit of radius r, with an angular velocity ω, is $W=2m\pi^2\omega^2r^2$, and since the angular momentum $2\pi m\omega r^2=\frac{1}{2}nh/\pi$, it follows on substituting for ω, $W=n^2h^2/8\pi^2mr^2$; and remembering that $W/h=\nu$, it follows that the frequency of the lines in two states of the particle should be

$$\nu = \frac{h}{8\pi^2mr^2}(n_1^2-n_2^2)$$

which is similar in type to H. Deslandres' formula, when n_1 and n_2 are integers corresponding with two states of the molecule. The formula was further improved by allowing for the fact that molecules are not really rigid bodies. A. Sommerfeld, A. Eucken, H. M. Randall, E. S. Imes, W. W. Sleator, E. Gehrcke and L. C. Glaser, and W. Lenz have discussed the application of the quantum theory to band spectra.

The action of a magnetic field on spectral lines.—P. Zeeman [4] found that when the light from a Bunsen's flame coloured with lithium carbonate or sodium flame is passed between the paraboloidal poles of an electromagnet, the spectrum,

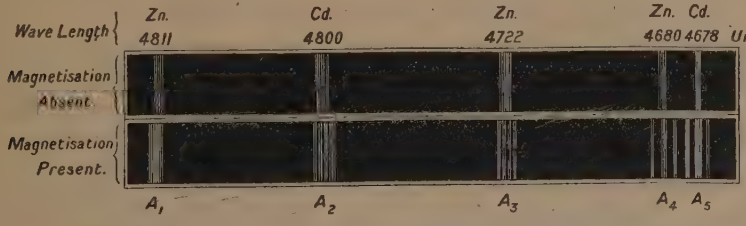

FIG. 3.—Effect of Magnetic Field on the Spectral Lines of Zinc and Cadmium—Zeeman's Effect.

with a grating of 14,938 lines per inch, showed that the two sodium lines, or the red lithium lines, are widened every time the current was turned on, and narrowed when the current was cut off. The sodium lines were widened on both sides to about $\frac{1}{40}$th of the distance between the lines when in a magnetic field of an intensity of about 10^4 C.G.S. units. In general, the lines in the normal spectrum of an element are usually broadened into doublets, triplets, sextets, octets, or still more, complex groups when in an intense magnetic field. The effect will be evident from Fig. 3. Different lines of the elementary spectra are perturbed in different ways—some lines, originally single, may remain single ; others give rise to doublets,

triplets, quartets, octets, etc. There is a certain pathetic interest attaching to this phenomenon—called the **Zeeman effect**—because the last experiment made by M. Faraday (March 12, 1862) was an attempt to find if any spectral change could be detected when the source of the light is placed in a magnetic field.

> The colourless gas flame ascended between the poles of the magnet, and the salts of sodium, lithium, etc., were used to give colour. A Nicol's polarizer was placed just before the intense magnetic field, and an analyzer at the other extreme of the apparatus. Then the electro-magnet was made, and unmade, but not the slightest trace of effect on or change in the lines in the spectrum was observed in any position of polarizer or analyser.

Observations by A. Trève, A. J. Angström, L. Daniel, A. Secchi, J. Chautard, E. van Aubel, and P. Thènard were also abortive. In 1886, C. Fievez noted that the spectral lines of a flame were broadened in a magnetic field. He said: Les phénomènes qui se manifestent sous l'action du magnétisme sont identiquement les mêmes que ceux produits par une élévation de temperature. M. Faraday's experiment failed because the only available magnet was not strong enough. **The perturbation of the spectral lines in a strong magnetic field is supposed to be due to alterations in the mode of vibrations of the subatomic particles under a magnetic stress.** The observed displacement depends on the strength of the magnetic field. If the spectrum be produced by the vibration of atoms of the same kind, it would be difficult to explain why the mode of vibration of atoms of the same kind can be altered in this way. It is more reasonable to suppose that **the different effects produced by a magnetic field on the different lines of the spectrum of a substance are due to the presence of different kinds of particles in the incandescent element.** This simply means that at the high temp. of the luminous object, the atoms of the element are dissociated into simpler sub-atoms, which are probably electrified. Owing to the fact that corresponding lines in the spectra of related elements—for instance, magnesium, zinc, cadmium—are similarly affected so that the groups of lines in the different spectra undergo the same modification, it is inferred that the vibrating corpuscles which produce the A_1, A_2, A_3, . . . lines in the spectrum of zinc are the same as the vibrating corpuscles which produce the A_1, A_2, A_3, . . . lines in the spectrum of cadmium, etc. Hence, not only is an atom a complex association of different corpuscles, but the atoms of allied elements probably contain certain groups of corpuscles, or sub-atoms, in common. "These observations," said T. Preston, "lend some support to the idea so long entertained merely as a speculation, that all the various kinds of matter, all the various so-called elements, may be built up in some way of the same fundamental substance."

The phenomenon has been studied by A. A. Michelson, T. Preston, A. Cornu, H. Becquerel and H. Deslandres, A. Cotton, A. Righi, C. Runge and F. Paschen, S. Popow, F. Paschen and E. Back, P. Ehrenfest, J. M. Burgers, and P. Debye. In general, (i) the lines of band spectra are not influenced by a magnetic field; (ii) the lines may be resolved into twins or triplets—a greater number may be obtained; (iii) the different lines belonging to the same element are not all affected in the same way; (iv) with related elements the related lines behave in a similar way; (v) the magnitude of the effect is proportional to the intensity of the magnetic field. H. A. Lorentz, W. Voigt, A. Sommerfeld, H. A. Kramers, N. Bohr, and K. F. Herzfeld have developed the theory of the main features of the Zeeman effect. A. Sommerfeld, P. Das, etc., applied the quantum theory to Zeeman's effect. Assuming that light is produced in the atom by electrons oscillating about a positive nucleus—*vide infra*—it follows that the frequency of this vibration should be affected by a magnetic field because the latter must oppose or aid the centripetal force which is exerted by the positive nucleus on the rotating electron according as the direction of rotation is clockwise or anti-clockwise with respect to the lines of magnetic force. Hence, instead of a one-line spectrum two or three lines are produced, the two outer ones being produced by the vibrations of electrons whose orbits are deflected right and left with respect to the lines of magnetic force. The

central line has the same frequency as that of the original line, because it is produced by electrons whose orbits are situated in a plane parallel to the direction of the lines of magnetic force. The values of the ratio e/m are computed from $2(\nu_1-\nu_2)\pi V^2/H=e/m$, deduced by H. A. Lorentz. Here ν_1 and ν_2 refer to the vibration frequency of the two outer spectral lines; V denotes the velocity of light; and H is the strength of the magnetic field. The results so obtained agree well with those obtained by measurements on the cathode rays.

The action of a magnetic field on polarized light.—A similar explanation applies to the observed rotation of the plane of polarized light by a magnetic field, first observed by M. Faraday,[5] and hence called the **Faraday effect.** The effect has been the subject of numerous investigations. The influence of temp. has been investigated by E. Bichat,[6] etc.; and the influence of chemical composition by W. H. Perkin,[7] etc.

The action of an electric field on spectral lines.—Prior to 1913, no one had been able to show that an intense electric field had any influence on the spectral lines. A gas is always an electrical conductor when it is emitting a spectrum; there was therefore a difficulty in maintaining a sufficiently intense electric field to obtain a measurable displacement. J. Stark,[8] however, succeeded in applying an electric field to a beam of canal rays and found that with hydrogen each line was resolved into a number of components which increased with the frequency of the line. Similar results were obtained with helium. The phenomenon is known as the **Stark effect.** Almost simultaneously, and yet independently of J. Stark, L. Surdo also succeeded in observing the effect in the cathode dark space of a discharge tube. The theory based on the atoms embodying positive nuclei each with a set of revolving electrons was worked out by K. Schwarzschild, and P. S. Epstein. The subject is discussed by A. Sommerfeld, L. Silberstein, and N. R. Campbell. G. Hettner shows that if the diatomic molecules of a gas have an electrical moment, there should be a shift and a splitting of the spectral lines in the external electrical field.

In **absorption spectra,** it is supposed that light is absorbed by the body, and that some particles are stimulated into sympathetic vibration, so that they vibrate about a position of equilibrium. P. Drude [9] assumed that every molecule contains a number of electrons equal to the sum of the valencies of the atoms in the molecule, and also an ion or ions with a total positive charge equal to the sum of the negative charges. He showed that the harmonic vibration of electrons causes an absorption band, and influences the index of refraction in the neighbourhood. The periods of vibration of the electrons were assumed to be in the ultra-violet, and those of the ions or charged atoms in the infra-red. R. A. Houstoun derived a formula for m/e from the variation of the absorption coeff., and found it agreed in some cases with values of that ratio derived from other sources. Hence, he inferred that the absorption spectra of such soln. is produced by the vibrations of interatomic electrons; with aq. soln. of cobalt chloride, and uranyl nitrate, the results agreed better with the assumption that the vibrating particles have atomic dimensions. With cobalt chloride in aq. soln. it is supposed that the positively charged cobalt atom vibrates harmonically with the negatively charged chlorine atoms under the influence of electrical attractions. If, however, cobalt chloride be ionized the vibration of the cobalt atom will cease, and the cobalt ion cannot have a spectrum unless it be supposed that the vibrations occur inside the atom (electrons), or that the cobalt ion has surrounding water molecules.

The spectra of stars and nebulæ.—The nature of the spectrum of an incandescent body depends upon the temp.; and since the spectra of many elements have been observed at several different temp., it is possible to get a rough idea of the temp. of any incandescent element from the appearance of its spectrum. For instance, the flame spectrum of sodium has two yellow lines close together, while the spark spectrum has a pair of lines in the orange and in the green; the flame spectrum of thallium has a single green line, and the spark spectrum has in addition

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some bands in the violet. This fact is explained by the assumption that at the higher temp., the atoms of an element are aggregates of sub-atoms, each of which has its own characteristic mode of vibration. The spectra of the nebulæ, stars, and suns thus enable rough approximations of their temp. to be made.

The sun, stars, and nebulæ, said A. M. Clerke,[10] form so many celestial laboratories where the nature and mutual relations of the chemical elements may be tried by more stringent tests than sublunary conditions afford. Astronomers tell us that the nebulæ are the material out of which stars are made, and that in their forms, aggregations, and condensations, the process of evolution of stars and suns can be traced. The nebulæ begin either as hot attenuated gases or as clouds of cold meteoric stones which gradually gain heat as they clash together, until finally they are converted into gases, and then gradually cool by radiation. Hence, the cooler stars are either young or old, heating up or cooling down. The hottest stars are in their prime. In the very hottest stars with an estimated temp. of 25,000°—*e.g.* β-Crucis—comparatively few chemical elements can be detected, while in the cooler red stars—*e.g.* Betelgeuse—the number of spectral lines is comparatively large, and a large number of elements are present. New elements appear to be introduced at each stage in the cooling of hot stars, so that elements which were non-existent in the hotter stars make their appearance in the cooler stars; and a few elements disappear in passing from the hot to the cooler stars.

In the hotter stars little more than hydrogen can be detected, then follow hot stars with calcium, magnesium, and a few other elements superadded; then come cooler stars with more complex spectra corresponding with a greater variety of elements. The planets, of which our own is a type, are among the cooler orbs. If the different suns and stars be arranged in a series, **the order of the appearance of the elements in the cooling stars is approximately the order of their increasing complexity as deduced from the magnitude of their atomic weights.** The lightest elements alone appear in the hotter stars. These facts fit very well into the hypothesis that the matter of which stars are made, passes through a real change in the nature of the constituent elements, and that there is a progressive tendency of the elements to assume more stable forms in passing from the hotter to the cooler stars. This corresponds with the assumption that the atoms are built of particles which form more and more complex aggregates as the temp. falls. Carbon is an exception. It has a low at. wt., and yet it appears comparatively late, but the non-volatility of the solid element shows that the molecule is probably complex. Calcium (at. wt. 40) appears before sodium (at. wt. 23); this may be due to the fact that the stability of the system of corpuscles which form an atom not only depends upon the number but also upon the mode of arrangement of the corpuscles. In a general way, however, the elements appear in the cooling stars in the order of their increasing at. wt. The stars may thus be arranged in groups corresponding with different stages in their development. The hydrogen-helium stars pass by insensible gradations into stars of the solar type, and finally into the deep red stars. This is illustrated by Table II, due to J. N. Lockyer.

TABLE II.—STELLAR TEMPERATURES.

	Spectrum.	Temperature.	Appearance of the elements.
Gaseous stars .	Longest	Highest	Hydrogen, helium, asterium (a gas not known on earth).
Metallic stars .	Medium	Medium	(*a*) Feeble spectrum of helium and hydrogen; magnesium; calcium; silicon and oxygen. (*b*) No gases of the helium family; iron; manganese; nickel; copper; etc.
Carbon stars. .	Shortest	Lowest	Carbon and compounds of carbon.

Astronomers consider that the different stages in the evolution of sidereal systems cannot be demonstrated by the slow cooling of a *single* star, because the span of human life relative to the duration of cosmical events is far too short to enable the different stages to be followed in succession; these different stages can rather be followed by arranging the different nebulæ in a series so as to show all gradations, from a diffuse luminous haze to stars with faint nebulous halos. The spectra of the gaseous and presumably younger nebulæ consist of three lines corresponding with hydrogen, helium, and some unknown elements—the great nebula in Orion is usually given as an example. As the nebulæ grow older and more compact, more lines corresponding with other elements appear. These spectra are supposed to represent clusters of corpuscles more stable than the rest. Hence, according to **J. N. Lockyer's evolution hypothesis,** the spectra of a properly arranged series of stars and nebulæ indicate that **the chemical atoms have grown during the cooling of the primal ultra-atomic gas much as visible rain drops grow from invisible water vapour.** Before hydrogen appeared, a whole series of lighter elements were probably formed by the gradual condensation (polymerization, etc.) of the cooling "fire-mist," and then passed into the heavier and more complex elements as the temperature fell still lower. From a chemical point of view, therefore, the cooling of the primal matter has resulted in the formation of a succession of polymers $(1, 2, 3, \ldots)\eta$, where η is the density of the hypothetical protyle. The polymerization may also proceed in successive stages. $A=(1, 2, 3, \ldots)x$; $B=(1, 2, 3, \ldots)y$; $C=(1, 2, 3, \ldots)z$; . . . where $x, y, z, \ldots$ represent the densities of simple forms of matter. These complexes unite to form the series:

$$An, Bm, Cp, \ldots; AB, BC, \ldots; ABC, \ldots$$

where $n, m, p, \ldots$ are integers. The light elements—*asterium, coronium, nebulium,* etc.—which appear to be present in some of the more attenuated nebulæ, and in the hotter stars, have probably long since vanished from the earth. We infer their existence from their characteristic spectra. Helium was once included in the list of light stellar elements unknown on earth.

There is not much room for doubt about the theory with respect to the cooling of hot stars, but with nebulæ, S. Arrhenius considers that the great *cold* reigning in space has condensed all but the lighter elements into solid or liquid state, and these have gravitated to the interior. The outer layer only is rendered luminous by dust particles and corpuscles flying into the nebula from space.

The hypothesis which is supposed to correlate these and other facts, is as follows: Long before the earth was formed, it is supposed that a kind of ultra-gaseous protyle was suffused throughout space, and, what has been called the temp. of the protyle, was inconceivably hotter than anything at present known on earth. In course of time, some process, akin to cooling, reduced the temp. of the protyle so that it was condensed into material atoms. The simplest elements most nearly allied to the protyle would naturally condense first—thus, hydrogen and helium with their low at. wt. were born. Then followed the elements next in order of complexity until finally uranium or radium was born. We do not know an element with a greater at. wt. and presumably a more complex structure. If the ideas developed in the chapter on the architecture of the atom approximate to the truth, even this element is not stable, and is slowly breaking down into simpler more stable forms. As the temp. fell still lower, the earlier formed elements would unite among themselves and produce chemical compounds. It is possible to reverse the process and dissociate chemical compounds by elevating the temp., but it has not been possible to raise the temp. high enough to verify the hypothesis by dissociating the elements.

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§ 4. Electric Discharges in Attenuated Gases

If a first step towards understanding the relations between æther and ponderable matter is to be made, it seems to me that the most hopeful foundation for it is knowledge derived from experiments on electricity in high vacuum.—Lord Kelvin (1893).

The study of the phenomena attending the passage of electricity through gases has led to astounding developments during the past twenty years, and abundantly justified Lord Kelvin's prognostication. Under ordinary conditions, gases are such poor conductors of electricity that they are classed as good insulators. In order to get electricity to pass through air at ordinary atm. press., an electrical press. approaching 30,000 volts per cm. is required ; and as the press. of the air is diminished the voltage required to produce a discharge diminishes in almost exactly the same proportion. If a glass tube, about 30 cm. long, Fig. 4, be connected with a mercurial air pump, and the aluminium electrodes—disc and point—be connected with an ordinary induction coil and battery, either no spark, or thin zig-zag sparks will pass through the tube ; all depends on the distance of the electrodes apart, and on the electric press. produced by the coil. If the pump be started, the spark passes more and more readily as exhaustion proceeds ; first, forked brush-like bluish sparks begin to leap from electrode to electrode ; when the press. reaches

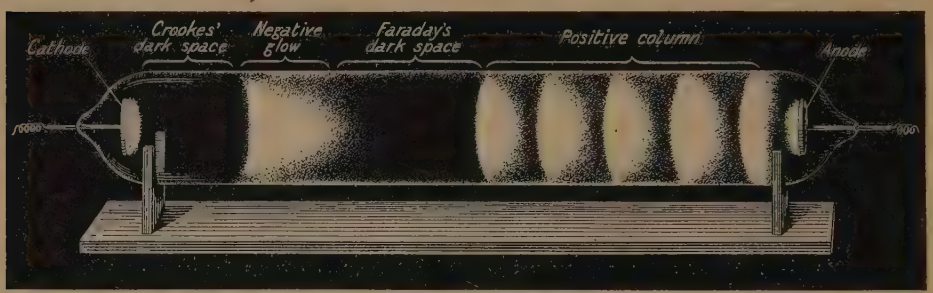

Fig. 4.—The Effect of an Electric Discharge on Attenuated Gases.

40 mm. of mercury, a luminous red streamer appears ; the red line widens, forming a fuzzy strip between the electrodes ; when the exhaustion is such that the press. is about 10 mm., a luminous band fills the whole tube, and a violet halo surrounds the two electrodes. At 6 mm. press., the band begins to break up into layers ; at 3 mm. press., the tube appears to be filled with a number of transverse flickering reddish striæ, alternately light and dark. Glass tubes of about this degree of exhaustion—Geissler's tubes—are made in numerous patterns, and with different kinds of glass so as to get different fluorescent effects. Tubes containing gases under reduced press. and arranged for the passage of an electric discharge are called *vacuum tubes*. As exhaustion proceeds, the violet haloes about the electrodes grow larger and larger, and, as M. Faraday [1] noted in 1838, a dark space—**Faraday's dark space**—appears at the negative electrode. The prevailing colour of the pulsating striæ depends on the nature of the gas in the tube—with hydrogen the colour is red, and with chlorine green. The auréole about the cathode—called the **negative glow**—separates from the flickering striæ, and a dark space—**Crookes' dark space**—appears between the negative glow and the cathode, Fig. 4. This was observed by J. Plücker in 1858, and described by W. Crookes in 1879. The luminous striæ stretching beyond Faraday's dark space is called the **positive column.** The length of Crookes' dark space, the negative glow, and Faraday's dark space do not depend very markedly on the length of the tube ; in long tubes the positive column occupies most of the tube—for example, in a tube 2000 cm. long, the positive column may occupy all but about 3 cm. As the exhaustion continues, the striæ diminish in

number and size; and they appear to be paler in colour. The light at the anode dwindles down to a luminous point, and Crookes' dark space at the cathode soon expands, and finally fills the tube. The glass then acquires a greenish-yellow phosphorescent light if the tube is made of soda glass. The press. is then about 0·33 mm. of mercury. J. Plücker first observed the walls of the discharge tube near its cathode glowed with a phosphorescent light. With further exhaustion the tube looks as if it were empty, but the glass still glows brightly, particularly about the cathode. With still further exhaustions, the current from the induction coil is unable to pass through the vacuum tube. The fact that the tube when highly evacuated is non-conducting shows that *the electric current must somehow be carried from one electrode to the other by something*, otherwise action at a distance is possible.

J. Stark and W. Hermann,[2] E. Goldstein, E. Wiedemann and A. Pospieloff, W. Matthies, E. Gehrcke and R. Seeliger, etc., have investigated the colour and spectra of the negative glow with various gases and vapours. The negative glow with *hydrogen* is bluish-white and it shows two spectra and Balmer's series; with *nitrogen* the colour is violet-blue, and it shows band and line spectra; with *helium* the colour is green, and with *argon* blue, while both show line spectra; with *neon* the colour is red; with *oxygen* the colour is greyish or yellowish-white, and it shows a band spectrum; with *carbon monoxide* the colour is greyish-white, and there is a band spectrum; with *carbon dioxide*, the colour is sky-blue; with *chlorine* the colour is green, yellowish-green with *bromine*, and orange-yellow with *iodine*, bromine and iodine give a band spectrum. With *sodium* the colour is yellow, and it gives the *D*-line; with *potassium* the colour is pale blue, with *rubidium* blue, and with *cæsium* greenish or greyish-white, and all give line spectra; with the vapours of *cadmium* and *zinc* the glow is red, and there are line spectra; and with *mercury* vapour, the colour is green or white, and it gives a line spectrum.

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§ 5. Cathode and Lenard Rays

The electron has conquered physics, and many worship the new idol rather blindly.—H. POINCARÉ (1907).

Whoever rejects faith in the reality of atoms and electrons, or the electro-magnetic nature of light waves, or the identity of heat and motion, cannot be found guilty of a logical o rempirical contradiction; but he will find it difficult from his standpoint to advance physical knowledge.—M. PLANCK (1913).

W. A. Hittorf[1] showed that if a solid body—say a Maltese cross made of mica—be placed between the anode, *A*, and cathode, *C*, as in Fig. 5, a true shadow appears on the glass when the tube is evacuated; the shape of the cross shows that something must travel from the neighbourhood of the cathode in straight lines. This "something" which causes the phosphorescence of glass was called by E. Goldstein *Kathodenstrahlen*—**cathode rays.** Hence, (1) *the cathode rays travel in straight lines normal to the surface of the cathode; and they will cast a well-defined shadow if a solid object be placed between the cathode and the wall of the vacuum tube.* The experiment can be varied in an ingenious manner, as shown by W. Crookes, Fig. 6, by arranging the stream of cathode rays so that it strikes the upper vanes of a little paddle wheel which then rolls horizontally along a pair of parallel glass rails, away from the cathode. By

reversing the electric current, the wheel stops and then revolves in the opposite direction owing to the fact that the direction of the cathode stream has been reversed. Hence, (2) *cathode rays can exert mechanical pressure.* By directing the cathode rays on to different minerals, W. Crookes showed that beautiful phosphorescent effects may be obtained. Crystals of perthite, and didymium glass give a red phosphorescence; artificial rubies, and willemite a green phosphorescence; scheelite, yellow; Iceland spar, white; barium platinocyanide, zinc blende, etc., also glow and phosphoresce when exposed to the rays. Hence, (3) *many minerals become phosphorescent when exposed to the cathode rays.* The spectra of phosphorescent

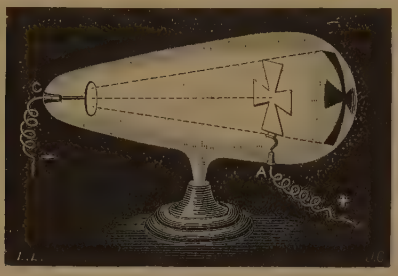

FIG. 5.—Shadows Cast by Cathode Rays.

FIG. 6.—Mechanical Motion by Cathode Rays.

rare earths are of great value in studying these compounds. E. Wiedemann and G. C. Schmidt found that even when no visible coloration is produced by the cathode rays, a body after exposure is often so changed that when, subsequently weeks or even months afterwards, it is warmed it becomes luminous—thermo-luminescence—at a temp. far below that at which it becomes luminous in the normal state. There is sometimes, also, an after-glow which lingers for a time after the bombardment has ceased. E. Wiedemann and G. C. Schmidt's results are indicated in Table III. W. Crookes also showed that the cathode stream, when focussed

TABLE III.—EFFECT OF CATHODE RAYS ON VARIOUS SALTS.

Substance.	Cathode phosphorescence.	After-glow.	Thermo-luminescence.
$CaSO_4$ . . .	Faint yellowish-red	None	None
$CaSO_4(-MnSO_4)$.	Intense green	Strong green	Intense green
$SrSO_4$ . . .	None	—	—
$SrSO_4(-MnSO_4)$.	Bright red	Perceptible	Perceptible
$BaSO_4$ . . .	Faint dark violet	—	—
$BaSO_4(-MnSO_4)$.	Dark blue	Faint	Very faint
$MgSO_4$ . . .	Red	Perceptible	Feeble
$MgSO_4(-MnSO_4)$.	Intense dark red	Persistent	Intense red
$ZnSO_4$ . . .	Bright white	Persistent	White
$ZnSO_4(-MnSO_4)$.	Intense red	Very persistent	Very strong red
Na_2SO_4 . .	Bluish	Faint	Bright
$Na_2SO_4(-MnSO_4)$.	Intense brownish-yellow	Strong	Bright yellow
$CdSO_4$ . . .	Yellow	Persistent	Bright yellow
$CdSO_4(-MnSO_4)$.	Intense yellow	Very persistent	Intense yellow
CaF_2 . . .	Faint bluish	Very faint	Faint
$CaF_2(-MnF_2)$.	Intense yellow	Persistent	Intense green

on platinum by means of a cathode shaped like a concave mirror, may heat the metal white hot, glass can be melted, diamonds charred, etc. Hence, (4) *the cathode rays raise the temperature of bodies on which they fall.* Measurements of the heat developed by the rays have been made by E. Wiedemann and co-workers, P. Ewers, etc. E. Goldstein found that if the cathode stream be allowed to impinge on white rock-salt or lithium chloride these salts are coloured violet. The glass of the vacuum

tube is also coloured after long use. E. Wiedemann and G. C. Schmidt, J. Elster and H. Geitel, etc., have investigated this subject. P. Villard found that cathode rays exert a reducing action on cupric oxide. It is not always easy to distinguish chemical effects produced by the incidence of the rays from the secondary effects due to the heat produced by the rays. Platinum acquires a film of platinum black after long exposure to the rays. Hence, (5) *the cathode rays can produce chemical and physical changes.* H. von Helmholtz noted that a point discharge on a jet of steam results in the condensation of drops of water; F. Richarz found that condensation of steam is produced by the action of an electrical discharge. J. S. Townsend showed that electrified gases produce a fog when admitted into a vessel containing aq. vapour; and C. T. R. Wilson found that if a stream of electrons be directed into an atm. of moist air, each electron serves as a nucleus about which moisture collects, and each electron becomes the centre of a visible drop of water. Hence, (6) *a stream of electrons, when directed into moist air, forms a cloud.* The cloud or mist is an aggregate of minute falling raindrops; and it is assumed that, like a particle of dust in moist air an electron in moist air can serve as a nucleus for the condensation of the water vapour. E. Goldstein showed that the cathode rays can be reflected when they strike a surface at various angles of incidence. L. W. Austin and H. Starke found for the different metals of sp. gr. D the percentage amounts R of the incident rays which are reflected:

	Pt	Pb	Ag	Bi	Ni	Cu	Fe	Zn	Al	Mg
R	72	63	59	54	48	45	43	40	25	25
D	21·5	11·3	10·5	9·9	8·9	8·5	7·7	7·1	2·6	1·7

The proportion of cathode rays reflected is roughly proportional to the square root of the sp. gr. of the metal. W. Seitz measured the percentage reflection with different angles of incidence of the cathode rays; A. Becker, A. A. C. Swinton, H. Starke, E. Wiedemann and P. Ewers, W. Cady, P. Ewers, E. Merritt, E. Gehrcke, G. E. Leithäuser, S. Williams, etc., have studied the reflected cathode rays. The diffusion of the cathode rays was investigated by P. Lenard, J. Robinson, etc. M. E. Tressler has discussed the uses of the cathode rays, and J. J. Thomson the uses of electrons.

In 1895, J. Perrin arranged a vacuum tube so that the cathode stream passed into a small metal cylinder inside the tube, and, by means of a wire, he connected the inner cylinder with an external electroscope. The electroscope acquired a gradually increasing negative charge, or a positively charged electroscope was discharged. Hence, (7) *the cathode rays are negatively electrified while the other contents of the tube are positively electrified.* E. Goldstein, W. Crookes, and E. Wiedemann and H. Ebert studied the mutual deflection of two cathode streams in the vicinity of one another. J. Plücker showed (8) *the cathode rays can be deflected from their normal course by means of a magnet.* This is illustrated by Fig. 7, for if a magnet be directed to the side of the tube through which a discharge is passing, the focus of the rays can be deflected on to the walls of the tube. The heat produced by the bombardment of the walls of the tube by the cathode stream will suffice to melt a little wax placed on the outside of the tube. A. K. Birkeland found that the cathode rays are not only deflected by a magnet, but they are also broken up into several distinct patches or groups, giving a kind of magnetic spectrum studied by R. J. Strutt, J. J. Thomson, etc.

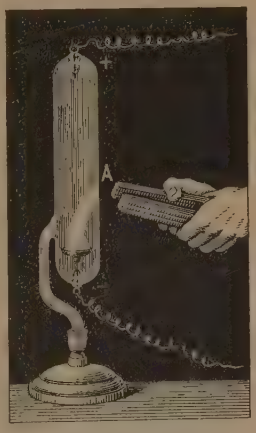

FIG. 7.—The Effect of Magnet on Cathode Rays.

H. Hertz found that when thin films of gold leaf or aluminium are interposed in the track of the cathode rays, they show an appreciable phosphorescence on the

reverse side of the plate, thus indicating that the cathode rays are in part transmitted through the thin metal. P. Lenard made a tube with a thin aluminium sheet—*D*, Fig. 8—carried by a brass cap, at the end opposite the cathode *C*; a metal cylinder, *A*, served as anode. P. Lenard found that the cathode rays passed through the aluminium window outside the tube; they were then called **Lenard rays.** The cathode or Lenard rays are absorbed by different metals used as windows—the absorptive power of a substance is almost directly proportional to its density. If the metal window is too thick, the cathode stream is arrested. Hence, (9) *the cathode rays can penetrate and pass through thin sheets of metal, but not through thick sheets.* The subject was studied by W. Seitz. The loss in velocity of cathode rays in passing through thin metal plates was studied by G. E. Leithauser and T. Descoudres. P. Lenard measured the absorptive power of different substances for the cathode rays, and expressed the absorption, *A*, in terms of the amount absorbed by a layer of substance of 1 sq. cm. section and 1 grm. in weight.

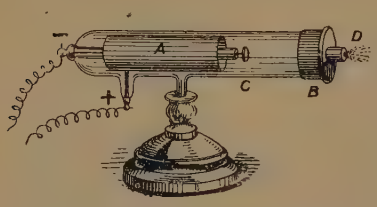

FIG. 8.—Lenard's Tube to bring the Cathode Rays outside the Vacuum Tube.

	H (3·3 mm.)	H (760 mm.)	Air (0·78 mm.)	Air (760 mm.)	SO_2 (760 mm.)	Al	Mica	Ag	Au
A .	0·00149	0·476	0·00416	3·42	8·51	7150	7250	32200	55600
D . .	$0{\cdot}0_6368$	$0{\cdot}0_4849$	$0{\cdot}0_6125$	0·00123	0·00271	2·70	2·80	10·5	19·3

The ratio *A*/*D* is roughly 3200 (mean). Measurements were made by A. Becker, W. Kaufmann, etc.

C. F. Varley suggested that the cathode rays are composed of "attenuated particles of matter, projected from the negative pole by electricity," and in virtue of their negative charges, these particles are affected by a magnet. About eight years afterwards, W. Crookes suggested that they were particles or mols. of a **fourth state of matter**—an ultra-gaseous state which was called **radiant matter**—in which the free paths of the mols. were so long that collisions could be disregarded. W. Crookes showed that the so-called Crookes' dark space at very high exhaustions may occupy the whole tube, and he suggested that the thickness of this dark space may be a measure of the mean length of the free path of the particles. "The extra velocity with which the mols. rebound from the excited negative pole keeps back the more slowly moving mols. which are advancing towards that pole. The conflict occurs at the boundary of the dark space when the luminous column bears witness of the energy of the collisions. He attributed the fluorescence of the walls of the tube to the impact of the particles on the glass. W. Crookes' idea was that the cathode rays are ordinary gaseous mols. carrying electric charges, and in which the free path is so long that collisions may be disregarded. E. Wiedemann, E. Goldstein, H. Hertz, etc., did not accept the molecular torrent theory of the cathode rays, but regarded them as due to disturbances in the æther.

Owing to their high penetrative power (Lenard rays), and the fact that no difference in the properties of electrons can be detected by changing the kind of gas in the evacuated tube, or by changing the electrodes, it follows that (10) *the cathode rays are independent of the kind of matter present; and if the particles be matter at all, the matter is the same in kind, from whatever source it is derived.* In 1842, R. Phillips asked: May not electricity be an atomic compound minus some of the ordinary properties of matter? M. Faraday had previously answered (1835)

> The atoms of matter are in some way endowed or associated with electrical powers to which they owe their most striking qualities, and amongst them their mutual chemical affinity. . . . The equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity or have naturally equal electric powers; it being electricity which determines the equivalent number because it determines the combining force. Or, if we adopt the atomic theory or phaseology, then the atoms of bodies which

are equivalent to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them. But, I must confess I am jealous of the term *atom*; for although it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature.

W. Weber attributed electrical phenomena to the agency of stationary or moving charges which could be pictured as discrete and atomic; he said:

The relation of the two particles as regards their motions is determined by the ratio of their masses e and e', on the assumption that in e and e' are included the masses of the ponderable atoms which are attached to the electrical atoms. Let e be the positive electrical particle. Let the negative be exactly equal and opposite, and therefore denoted by $-e$ (instead of e'). But let a ponderable atom be attracted to the latter so that its mass is thereby so greatly increased as to make the mass of the positive particle vanishingly small in comparison. The particle $-e$ may then be thought of as at rest, and the particle $+e$ as in motion about the particle $-e$. The two unlike particles in the condition described constitute then an Amperian molecular current.

H. von Helmholtz revived the atomistic conception in 1881. He said:

The same definite quantity of either positive electricity moves always with each univalent ion, or with every unit of affinity of a multivalent ion. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity.

Likewise O. J. Lodge emphasized the same idea four years later. Lord Kelvin also said that Faraday's laws necessitate something atomic in electricity. E. Wiechert, and J. J. Thomson suggested the startling hypothesis that what W. Crookes called "radiant matter" or **the cathode rays, is a stream of negatively charged particles or corpuscles which have been formed by the disintegration of atoms of the gas in the vacuum tube.** The term **electron** was applied by G. J. Stoney to designate the unit or atomic charge of electricity. Nature, said he, presents us with a single definite quantity of electricity; for, in electrolysis, each chemical bond which is ruptured within an electrolyte, a certain quantity of electricity traverses the electrolyte, and this quantity is the same in all cases. It is now almost universally applied to the sub-atomic particles supposed to stream from the negative electrode when a discharge is passing through an attenuated gas. No difference can be detected in the corpuscles derived from different gases, and hence it is inferred that **the electrons are common constituents of all gases.**

According to hypothesis, the electric discharge in attenuated gases splits the atoms of the gas into positively and negatively charged electrons. **The cathode rays are a stream of negatively charged electrons sent from the cathode with a high velocity.** It is inferred that ordinary atoms are probably made of nothing but aggregates of sub-atomic particles—positively and negatively charged. J. Larmor said:

Electricity is atomic in nature. . . . Electrons are centres of strain in the æther. . . . Matter consists of clusters of electrons in orbital motion round one another.

Under ordinary conditions, the charges counteract one another and the atom is electrically neutral. By the action of an electrical discharge, negative electrons are supposed to be detached from the atom, leaving a residue with a positive charge, and called a **positive electron** or positive ion. If a negative electron attaches itself to a neutral atom, the latter will acquire a negative charge. In reviewing the evidence derived from the properties of cathode rays J. J. Thomson said: "The explanation which seems to me to account for the facts in the most simple and straightforward way is founded on the view of the constitution of the chemical elements which has been favourably entertained by many chemists." The view is that **the atoms of the different chemical elements contain different aggregations of particles of the same kind;** otherwise expressed, that a part at least of all atoms consists of electrons.

Although the sign and magnitude of the electric charge carried by an ion in the electrolysis of soln. is constant and invariable—the hydrogen ion is always positively charged, H^+, and the chlorine ion negatively charged Cl^-—J. J. Thomson has emphasized the fact that in the electrolysis of gases the signs of the charges carried by different atoms of the same element are not always the same, for hydrogen atoms may carry positive or negative charges. The atoms of the elements, however, have a specific attraction for the different charges, so that a hydrogen atom attracts a positive charge more powerfully than a negative charge, and a chlorine atom on the contrary attracts a negative charge more powerfully than a positive charge.

One C.G.S. electromagnetic unit of current is 10 amp.; one C.G.S. electrostatic unit of current $=\frac{1}{3}\times10^{-9}$ amp. One ampère $=\frac{1}{10}$th electromagnetic unit $=3\times10^{9}$ electrostatic units. One electromagnetic unit of quantity $=10$ coulombs. Hence, one electrostatic unit of current $=\frac{1}{3}\times10^{-9}$ coulombs, or one coulomb $=\frac{1}{10}$ electromagnetic unit $=3\times10^{9}$ electrostatic units. One electromagnetic unit of resistance is 10^{-9} ohms, and one electrostatic unit is 9×10^{11} ohms. Hence, one ohm $=10^{9}$ electromagnetic units $=\frac{1}{9}\times10^{-11}$ electrostatic units. One C.G.S. electromagnetic unit of press. $=10^{-8}$ volts, and one electrostatic unit of press. $=300$ volts. Hence, 1 volt $=10^{8}$ electromagnetic units $=\frac{1}{300}$ electrostatic unit. One electromagnetic unit of capacity $=10^{9}$ farads, and one electrostatic unit of capacity $=\frac{1}{9}\times10^{-11}$ farads. A microfarad $=10^{-6}$ farads.

Experiments have shown that in all probability the electric charge on an ion formed in the process of electrolysis, is the same as the electric charge of an electron. The ionic theory of electrolysis shows that atoms or groups of atoms carry electric charges which are integral multiples of the unit charge borne by an atom of hydrogen. The electric charge carried by 1·008 grm. of hydrogen is 96,540 coulombs. The number of atoms in a gram-ion of hydrogen is $6\cdot06\times10^{23}$. Hence, the unit charge per atom is $e=96540\div6\cdot06\times10^{23}=1\cdot57\times10^{-19}$ coulombs; but one coulomb $=10^{-1}$ electromagnetic units, or 3×10^{9} electrostatic units; hence, the charge on a univalent ion in electrolysis may be expressed as $1\cdot57\times10^{-20}$ electromagnetic units or $4\cdot78\times10^{-10}$ electrostatic units. *In electrolysis, the ratio of the charge, e, to the mass, m, of the hydrogen ion, e/m, is* $9\cdot654\times10^{3}$ *electromagnetic units per gram.* The charge on the electron is $4\cdot7\times10^{-10}$ electrostatic units, or $1\cdot56\times10^{-20}$ electromagnetic units, and for gases *the ratio of the charge, e, to the mass, m, of the electron, e/m, is* $1\cdot774\times10^{7}$ *electromagnetic units per gram.* Hence, $9\cdot654\times10^{3}\div1\cdot774\times10^{7}=\frac{1}{1840}$ nearly, meaning that the mass of a hydrogen ion is 1840 times the mass of an electron or negatively charged corpuscle; and therefore **the mass of an electron is $\frac{1}{1840}$th the mass of a hydrogen atom**—*i.e.* $8\cdot9\times10^{-28}$ grms.; its diameter is about $3\cdot7\times10^{-13}$ cms., whereas an atom of hydrogen has a mass, *m*, or about $1\cdot64\times10^{-24}$ grms. The diameter of a molecule of hydrogen is about 2×10^{-8} cms., so that compared with the atom, the electron has quite a microscopic size. The electrons travel with a velocity ranging from 10^{7} to 10^{9} cms. per sec., or nearly 90,000 miles per second. Their speed is dependent upon the intensity of the electrical force passing through the vacuum tube. A cathode particle travelling at this speed could go nearly twice round the earth in a second. The idea that the electrical condition of matter and its chemical activity depend upon the addition or removal of electrons from atoms of molecules has been incorporated with the ionic hypothesis, and with the modern theory of the structure of the atom. A. Günther-Schulze has discussed the condition of electrons in electrolytic ions; H. F. Mayer, C. Ramsaüer, P. Lenard, and H. Akesson, the reactions of gas molecules with free electrons.

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§ 6. Rontgen or X-rays

We shall never succeed in exhausting unmeasurable nature.—A. von Humboldt.

When the exhaustion of a vacuum tube is such that the tube is on the verge of becoming electrically non-conducting, and the glass opposite the cathode is brilliantly fluorescent, rays proceed from the fluorescent glass, *outside the tube* ; these rays—called **X-rays** or **Röntgen rays**—have quite different properties from the cathode or Lenard rays, because they will pass through glass, and they are not deflected by a magnet. In a typical X-ray tube, there are generally but not essentially two anodes ; one of these, called the *anticathode* or target, is arranged to collect the rays from the cathode and to reflect and focus the resulting X-rays outside the tube. Like rays of light, the Röntgen rays can be reflected, refracted, and polarized ; and they are not appreciably affected by the most powerful electric or magnetic fields as a stream of charged particles would be. **Röntgen rays are produced by the destruction of the cathode rays, and are formed when the cathode rays suddenly change their velocity ;** and conversely, as L. Simons showed, a substance bombarded by X-rays may furnish cathode or β-rays. Every substance when bombarded by electrons emits Röntgen rays—the glass walls of a vacuum tube, heavy metals like platinum or uranium, etc. W. Wolff [1] found that Lenard's rays are accompanied by some X-rays. The X-rays travel in straight lines with a velocity not far from that of light. It is supposed that Röntgen rays—like the rays of light, radiant heat, and electromagnetic waves—are due to pulses or waves set up in the æther by the impact of electrons on matter. It is all a question of frequency or wave-length. Table IV gives the wave-lengths of a number of radiations, so as to show the relation of the X-rays to other kinds of ray. Hence the wave-length of the X-ray is about a thousand times smaller than the wave-length of sodium light, and is comparable with the size of the atom.

When X-rays of sufficient penetrating power are made to impinge on a substance, the latter itself becomes a source of X-rays which are called **secondary X-rays.** In

TABLE IV.—WAVE-LENGTHS OF SOME RADIATIONS.

Radiation.	Wave-length in cm.
Electromagnetic waves of wireless telegraphy . .	3×10^{3} to 5×10^{4}
Longest heat waves known	6×10^{-3}
Infra-red spectrum	6×10^{-3} to $7{\cdot}5\times10^{-5}$
Red spectrum	6×10^{-5}
Green spectrum	5×10^{-5}
Violet spectrum	4×10^{-5}
Ultra-violet radiations	4×10^{-5} to 2×10^{-5}
Schumann's waves	10^{-5} to 2×10^{-5}
Röntgen rays	10^{-8} to 10^{-9}

general, the secondary rays have very different penetrating powers from the exciting or **primary X-rays.** Only a small proportion of the cathode rays are effective in producing primary X-rays; the general efficiency of the conversion is low, for the X-rays are but a small by-product of the energy transformations in the tube. A. S. Eve and S. H. Day estimate that of the energy supplied to an ordinary X-ray tube, about 0·005 per cent. is contained in the X-rays. J. J. Thomson deduced that the energy of an X-ray is proportional to the fourth power of the velocity of the exciting cathode ray; and this was confirmed by the experiments of R. Whiddington; but R. T. Beatty found that while the relation may hold good for primary radiations, it is not valid for the so-called characteristic radiations (*vide infra*), for which the energy$=0{\cdot}000051A\beta^{2}E$, where A denotes the at. wt. of the anti-cathode, β, the velocity of the cathode rays expressed as a fraction of the velocity of light (3×10^{10} cms. per sec.), and E, the energy of the parent cathode rays.

In his paper *Ueber eine neue Art von Strahlen*, the discoverer of the X-rays, W. C. Röntgen (1895) found that they can excite fluorescence on a paper-screen coated with barium cyanoplatinate, $BaPtCy_4$, or calcium tungstate, $CaWO_4$; they can fog a photographic plate; and make the air through which they pass a conductor of electricity. The quantity of charge carried by the ions of conducting air is not always the same. The sum of the charges of a given sign carried by all the ions is often used as a measure of the quantity of radiation which has produced the charge. Since the sum of the positive charges is equal to the sum of the negative charges, it is merely a matter of expediency which sign of charge is used in the measurement. The amount of ionization produced in a gas in a given time depends (i) on the inverse square of the distance from the excitor (E. W. B. Gill); (ii) on the difference of potential applied to the tube (W. Hillers); (iii) on the penetrating ability of the rays (R. K. McClung, and C. G. Barkla); (iv) on the nature of the gas (J. A. Crowther); and on the press. of the gas (W. Hillers, R. K. McClung, and C. G. Barkla); but is independent of the temp. of the gas (J. A. Crowther, and J. H. Clo). E. F. Perreau, and G. Athanasiadis found that X-rays affect the electrical resistance of a selenium cell in the same manner as light rays.

Certain uranium and other compounds exhibit fluorescence when exposed to the action of X-rays. The excited fluorescence has a longer wave-length than the exciting X-rays. When the intensity of the radiation is increased as by bringing the object closer to the source, the intensity of the fluorescence is increased. W. C. Röntgen did not find any simple relation between the potential difference applied to the tube and the amount of fluorescence, but the two variables were in some cases directly proportional. In all cases, under constant conditions, the intensity of the fluorescent light varied inversely as the square of the distance between source and object. C. Schuhknecht, and A. Dahms obtained a visible fluorescence with calcium oxide from marble (reddish); cadmium iodide (greenish); mercurous iodide (reddish); barium fluoride, fluoroiodide, cyanoplatinate (yellowish-green), and sulphide; lead sulphate, iodide, sulphide, chromate, carbonate, nitrate,

and acetate; and zinc sulphide (yellowish or bluish-green). The spectrum of the ultra-violet fluorescence was observed with fluorspar; scheelite; zinc sulphide; potassium, calcium, and barium cyanoplatinates; ammonium uranium fluoride; potassium uranium nitrate; lead sulphide; and zircon. The glass of X-ray tubes is coloured violet presumably due to the separation of colloidal manganese. Fluorspar is coloured an intense blue (with cathode rays the colour is violet); when strongly heated, the coloration disappears with thermo-luminescence. G. Holzknecht observed colour changes were produced in sodium chloride, potassium bromide, etc., by exposure to X-rays; H. Bordier and J. Galimard, and W. B. Hardy and E. G. Willcock observed that iodine separates from soln. of iodine in chloroform or benzene by exposure to X-rays. The action of X-rays on silver bromide photographic plates has been discussed by R. Luther and W. A. Uschkoff, L. Zehnder, E. Marx, L. Cramer, etc. In general, an increase in the current sent through the exciting tube hastens photographic action; while an increase in the penetrating power of the rays makes the action slower. W. C. Röntgen and J. O. Heinze found that two X-rays which produce equal effects on a fluorescent screen, do not always produce the same effect on a photographic plate; and R. Luther and W. A. Uschkoff thought that they detected a difference in the action of light and of X-rays on a silver gelatino-bromide plate. L. Baumeister and R. Glocker found the liberation of iodine from soln. of iodoform in chloroform is not proportional to the energy of the incident X-rays. G. Schwartz found that X-rays precipitate calomel from a mixture of ammonium oxalate and mercuric chloride; various chloroplatinates were found by H. Bordier and J. Galimard, and G. Holzknecht to change colour when exposed to X-rays; and H. A. Colwell and S. Russ found that starch is changed by X-rays into soluble starch and then into dextrin. A. Dauvillier attributes the chemical actions of the X-rays to the destruction of the negative ions; the slow electrons expelled neutralize the neighbouring positive ions, and the electronegative and electropositive elements are thus liberated in the atomic state, or their valence is reduced—*e.g.* $Cu^{\cdot\cdot}$ to $Cu^{\cdot}$. Serious pathological changes are produced by the long-continued exposure of parts of the body to X-rays, so that an operator must protect himself most carefully.

The X-rays have a remarkable power of penetrating substances opaque to ordinary light. The penetrating power of Röntgen radiations refers to the decrease in the energy of a pencil of the rays which occurs when the rays are allowed to impinge on a given solid. The **equivalent transparency** of a substance to X-rays is the mass in decigrams of a right cylinder of one sq. cm. base, which, when traversed by X-rays parallel to the axis, produces the same absorption as a cylinder of paraffin wax 75 mm. high and 1 sq. cm. cross-section. The **penetrating power** of X-rays is usually characterized by measuring their absorption in a sheet of aluminium of definite thickness. If 1, 2, 3, . . . similar sheets are successively introduced, each sheet absorbs the same fraction of what it receives, so that there is no scattering or transformation of the rays, and if I_0 denotes the intensity of the normally incident beam; I, that of the emergent beam; and k, the fraction absorbed by unit area and unit thickness—the so-called **linear absorption coefficient,** or the **specific opacity,** then, for a plate of thickness d, it follows that $I=I_0e^{-kd}$. If k is large, the rays are easily absorbed, and if k be small, the rays are very penetrating. Röntgen radiations with a low penetrative power, called *soft rays*, are emitted from a vacuum tube which has relatively much residual air. The supply of electrons is then plentiful; their speed is comparatively slow; and a current of comparatively low electromotive force is needed. Conversely, radiations with a high penetrative power, called *hard rays*, are emitted if the tube be very highly exhausted. The supply of electrons is then relatively small; their speed is comparatively high; and the necessary electromotive force is high. S. Ratner has discussed the hardening of X-rays tubes by prolonged use. For X-rays of average hardness, k lies between 4 and 8 $cm.^{-1}$, and for hard rays between 2 and 4 $cm.^{-1}$. If the absorption coeff. k be divided by the density D of the absorbent,

the ratio k/D is called the **mass-absorption coefficient**; it measures the absorption per unit mass for a normally incident ray of unit cross-section. This constant is more important because, as usually measured, the absorption is determined by mass alone. The sp. transparency of an element for X-rays of a definite hardness is a function of the at. wt., and is greater the smaller the at. wt. The absorption of X-rays has been studied by R. A. Houstoun, F. Butavand, R. Glocker, L. de Broglie, K. A. Wingardh, W. E. Williams and B. L. Worsnop, etc. J. L. Glasson found that the stopping power of an atom is proportional to $N^{\frac{4}{3}}$, where N is the at. number, rather then to $A^{\frac{4}{3}}$, where A is the at. wt.

The specific opacity, or its reciprocal, the eq. transparency of an element, for the X-rays is characteristic, and is independent of its state of aggregation, its temp., and whether it is free or compound. The property is therefore additive, so that if masses m_1, m_2, m_3, . . . of elements of sp. opacity O_1, O_2, O_3, . . . are present in a total mass M and sp. opacity, O, then E, then $MO=m_1O_1+m_2O_2+m_3O_3+$ . . . L. Benoist found that for X-rays of one definite quality, the sp. opacity decreases or the eq. transparency increases regularly with the at. wt., so that if either be plotted with the at. wt., the curve, Fig. 9, is obtained for X-rays of medium hardness. Each quantity of X-ray has its own particular curve; for instance, the dotted line, Fig. 9, is for soft rays. The curves can be used for estimating the at. wt. of an element. Each multiple of the combining wt. is used until one is found which lies on the curve. A. S. Eve and S. H. Day measured the absorption coeff. of soft, medium, and hard X-rays in air up to 100 metres for distances up to 10 metres, with soft rays, k=0·0010 to 0·0018; and k/D is 0·8 to 1·4; with medium rays, k=0·00040, and k/D=0·32; and with hard rays, k=0·00029 and k/D=0·023; and for distances between 40 and 60 metres, k=0·00029 and k/D = 0·23 for medium rays; and k=0·00014, and k/D=0·11 for hard rays. The absorption by 1 cm. of air is eq. to that by $\frac{1}{820}$ cm. of water.

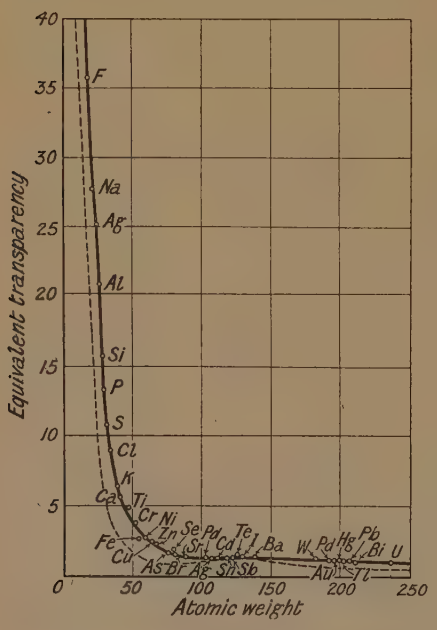

FIG. 9.—X-ray Transparency Curve of the Elements.

L. de Broglie gave $k\lambda^3N^4$ for the coeff. of at. absorption of the X-ray fluorescence, when N is the at. number. He also studied the thermodynamics of the absorption of X-rays. J A. Becker investigated the effect of a magnetic field on the absorption of X-rays. Various penetrometers and qualimeters have been devised for measuring the hardness of X-rays. The **reflection** of the X-rays has been studied by W. H. Bragg, C. G. Darwin, W. L. Bragg and co-workers, A. H. Compton, B. Davis and W. M. Stempel, H. A. Wilson, etc.

When the cathode rays strike the anticathode target, they are not arrested instantly at the surface, but merely suffer retardation, so that they penetrate for some distance into the body of the target. The particles travelling in the body are more or less deflected, and, if for a given velocity of cathode rays, the target be made thicker and thicker, a stage will finally be reached at which the particles travel uniformly in all directions; this critical thickness is called the depth of complete scattering. J. A. Crowther and W. R. Ham found the thickness with copper and with silver is 0·001 cm., with gold, 0·0020 cm., with aluminium is 0·015 cm., and with lead, 0·00025 cm., when the voltage is 90,000; but it varies

directly with the difference of potential across the tube. Those primary rays which are not absorbed by the target emerge into the vacuum space of the tube. C. G. Barkla and T. Ayres, and E. A. Owen studied the distribution of the scattered rays. C. G. Barkla found that if the difference of potential across the tube is small, the primary rays have a maximum intensity in a direction perpendicular to the cathode stream, and a minimum intensity parallel to that stream. The effect is called the *polarization of the X-rays.* As the difference of potential increases, the polarization decreases and finally vanishes. It is assumed that at the higher potentials the rays formed by the initial retardation of the cathode stream are negligible in their effects compared with those which come out in all directions from the depth of complete scattering. C. G. Barkla and J. G. Dunlop found the **coefficient of scattering,** s—defined in an analogous way to the coeff. of absorption k—is roughly proportional to the sp. gr. D, so that s/D is nearly constant 0·2. For elements of high at. wt., s/D increases slightly with at. wt. for hard rays and considerably so with soft rays. For a homogeneous radiation the absorption coeff. has to be amended to $s-k$. When a substance is exposed to a beam of X-rays, the emergent rays are scattered or deviated in direction, and the substance gives off so-called characteristic, monochromatic, or homogeneous X-rays. At the same time negatively charged corpuscular rays are formed. The scattered X-rays have been studied by C. G. Barkla and co-workers, J. A. Crowther, W. L. Bragg and co-workers, J. J. Thomson, C. W. Hewlett, T. E. van Auren, F. Dessauer and F. Vierheller, J. A. Gray, R. Blondlot, H. Haga, E. Bassler, J. Herwig, L. Vegard, W. R. Ham, F. C. Miller, etc. The rays emitted from an ordinary bulb are usually heterogeneous, both hard and soft, but C. G. Barkla and C. A. Sadler showed that radiators may be roughly divided into four groups:

Group 1, including the elements hydrogen to sulphur ranged in the order of their at. wt. When excited by a beam from a soft tube the members of this group give off little, if any, real secondary radiation, but rather a scattered radiation which is of the same nature as the exciting beam, and which is polarized in a plane perpendicular to the direction of the parent cathode stream. If the tube is made moderately hard, then a slight amount of true secondary radiation shows itself, and if the tube is very hard, a well-defined secondary beam is given off having a penetrating ability much different from that of the exciting rays.

Group 2, chromium to zinc. This group gives off a beam composed almost entirely of a true homogeneous secondary radiation even when excited by rays from a soft tube, but this radiation has little penetrating ability. With a given excitation, the ionization produced by it is almost 100 times that produced by an equal mass belonging to the first group.

Group 3, silver to iodine. If the exciting beam is only of moderate penetrating ability, this group gives off mostly a scattered radiation, but, unlike that from the first group, it is unpolarized, and there is a noticeable amount of true secondary radiation present. The relative amounts of scattered and secondary radiation vary greatly with small changes in the character of the exciting rays.

Group 4, tungsten to bismuth. These substances resemble group 2 in their action. For all the above elements the penetrating ability of the true secondary rays is independent of the intensity or of the penetrating ability of the exciting beam, but is a periodic function of the at. wt. of the radiating elements.

J. A. Crowther found that if the radiator is a chemical compound, the component atoms and radicals determine the character of the secondary rays produced. J. L. Glasson showed that the rays coming from salts are composed of (1) a homogeneous radiation having the same penetrating ability as that from the metal itself, and (2) a more penetrating scattered primary radiation due to the acid radical. If a metal occurs in the acid radical it has no individual effect, but merely acts along with the rest of the radical.

C. G. Barkla and C. A. Sadler showed that if the incident primary X-rays are less penetrating than the secondary radiations characteristic of a given radiator, no secondary rays are produced; but if the incident primary rays are more penetrating than the secondary radiation, secondary rays are produced. The analogy between the development of secondary X-rays with the production of fluorescent light has been emphasized by calling the former *fluorescent X-rays.* It was also

shown that if the **stimulus be great enough, every substance can be made to emit a set of X-rays which can be regarded as homogeneous and characteristic.** The quality of these characteristic rays depends on the substance and not on the exciting X-rays, provided the exciting rays are harder than the characteristic radiation. The penetrating power of these rays increases with the at. wt. of the metal from which they are emitted; and the characteristic radiation of an atom can excite the corresponding radiation of a lighter atom, but not that of a heavier atom. Under suitable conditions, many, possibly all, elements can emit at least two sets of characteristic radiations which C. G. Barkla distinguished as the **K-radiations** and the **L-radiations.** The former are about 300 times more penetrating than the latter.

In addition to the *K*- and *L*-homogeneous radiations, H. G. J. Moseley and C. G. Darwin, and W. H. Bragg found that platinum and some other metals give out a third type; M. Siegbahn observed an *M-series* with the elements of high at. wt. The mean wave-length of the *M*-series is four times as great as that of the *L*-series. J. Laub found that iron, copper, and zinc give what he called *I-series* of radiations, which with the metals named have k/D=43·9, 23·8, and 18·5 respectively. C. G. Barkla and M. P. White, C. M. Williams, and A. W. Hull and M. Rice observed discontinuities in the absorption coeff. of certain metals for X-rays of short wave-length, and they inferred the existence of a *J-series* of radiations. W. Duane and T. Shimizu observed no such discontinuity with aluminium, and F. K. Richtmeyer and co-workers obtained none with the other elements. It is therefore inferred that there is no evidence of *J*-radiations.

The greater the at. wt. of the metal emitting the *K*- and *L*-rays, the harder the rays. Elements with a high at. wt. readily furnish the *L*-radiation—this is the case with the elements ranging in the order of their at. wt. from zinc to uranium; and the *K*-radiations, from sodium to tungsten. According to R. Whiddington, and J. C. Chapman, there is a relation between the two series, in that if an element of at. wt. A_L has an *L*-radiation of a certain hardness, then the at. wt. A_K of an element whose *K*-radiation has the same hardness, is, $A_K=\frac{1}{2}(A_L-48)$. If this be correct, no element with an at. wt. less than 48 can have an *L*-radiation. Fig. 10 shows the relation between the at. wt. of the metal emitting the radiation and the mass absorption coeff. of the characteristic radiations in aluminium, including some γ-radiations from radioactive elements by E. Rutherford and co-workers. The observations of J. Chadwick and A. S. Russell, J. A. Gray, and H. Richardson are included in the diagram. If the logarithms of the two variables are plotted, two straight lines are obtained. E. A. Owen found that the penetrability of the radiations in aluminium are roughly proportional to the fifth power of the at. wt. of the metal emitting the radiation.

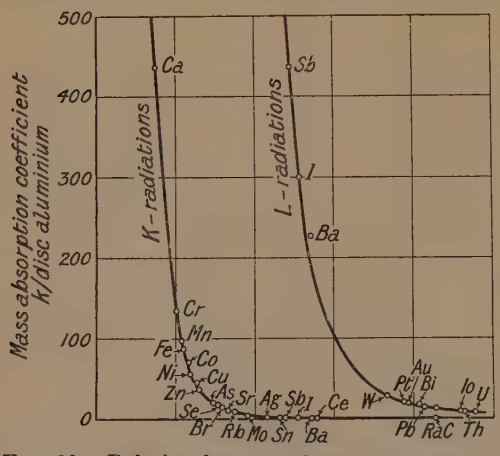

FIG. 10.—Relation between the Mass Absorption Coefficient of X-rays and the Atomic Weight of the Metal emitting the Radiation.

J. C. Chapman and co-workers, and J. L. Glasson showed that the characteristic X-rays are independent of temp. or of chemical combination. Ferric oxide, or sulphate, ferrosoferric oxide, and potassium ferrocyanide, all give iron rays of the same quality; tin nitrate similarly gives the tin rays; and methyl iodide and ethyl bromide vapours give characteristic iodine and bromine radiations when struck by hard X-rays. This shows that the X-ray phenomenon is purely atomic.

J. C. Chapman and S. H. Piper tried to find if the secondary radiation persisted

after the primary radiation has ceased, but not $\frac{1}{2\,5\,0}$th of the original radiation can be detected $\frac{1}{3\,0\,0\,0}$th of a second after the exciting primary rays were cut off. Since the primary rays from the target of an X-ray tube must pass through a certain thickness of the target before they can emerge, R. T. Beatty found as anticipated that such rays would excite that secondary radiation which is characteristic of the substance used as a target. There is some evidence to show that the cathode stream itself may cause the target to give off its characteristic radiation if the velocity of the cathode stream is large enough. W. R. Ham has been able, by the use of proper absorbers, to filter out the secondary rays coming from his tube, leaving only the primary rays. He found that the ratio of the secondary radiation to the primary was increased by an increase in the potential difference across the tube. The rays coming from an ordinary X-ray tube are therefore heterogeneous, and since the potential difference necessary to cause a discharge to pass through the tube varies with the condition of the tube this heterogeneity is constantly changing. X-ray spectra have been discussed by L. de Broglie, A. Dauvillier, G. Hertz, E. Gehrcke and E. Lau. F. C. Hoyt, J. E. Lilienfeld, G. Zecher, H. Behnken, N. Stensson, W. Kossel, A. Sommerfeld, M. Siegbahn, A. Smekal, E. Hjalmar, H. Fricke, W. Duane and R. A. Patterson, R. Whiddington, W. Duane and T. Shimizu, W. Duane and K. F. Hu, E. Hjalmar, W. H. Bragg, G. Wentzel, E. H. Kurth, J. A. Crowther, F. L. Mohler and P. D. Foote, D. Coster, etc.

If a correction be made for the scattering of the *K*- or *L*-series of X-rays which impinge on a metal, C. G. Barkla and C. A. Sadler showed that the ratio of the absorption by any two metals is approximately constant and is not dependent on the quality of the radiation, provided that such radiation does not excite the characteristic radiations of either metal. Thus C. G. Barkla and V. Collier found that the absorption by carbon for all types of X-ray is 0·11 when corrected for scattering—if not corrected, the absorption for soft rays is 0·11, and for hard rays, 0·41. G. W. C. Kaye studied the absorption of X-rays of various qualities of a particular metal, and found that the absorption decreases steadily as the rays are hardened, but the absorption reaches a minimum for rays identical in quality with the *K*- or *L*-characteristic radiations; and for rays a little harder than these, the absorption increases rapidly, and becomes permanently larger. C. G. Barkla and V. Collier also showed that the absorption of the X-rays from nickel increases steadily with the at. wt. of the absorbing metal so long as the *K*- and *L*-characteristic radiations are excited; when the at. wt. of the absorbing metal is so high that its *K*-characteristic ceases to be excited, the absorption suddenly drops. The increase is repeated until the *L*-radiation ceases to be excited, as shown in Fig. 11. E. A. Owen, and C. G. Barkla and V. Collier measured the absorption of characteristic X-rays by various gases and vapours—air, carbon dioxide, sulphur dioxide, ethyl bromide, and methyl iodide.

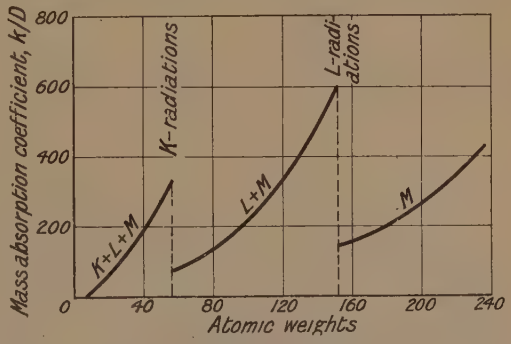

FIG. 11.—Relation between the Absorption of X-rays from Nickel and the Atomic Weight of the Absorbing Metal.

The X-rays are reflected by atoms in proportion to the at. wt. of the atoms struck. W. H. Bragg assumed the law of reflection to be $n\lambda=2d \sin \theta$, a formula which he employed in his study of the action of X-rays on crystals—**1.** 11, 8 E. Hjalmar, and P. P. Ewald have studied the accuracy of the formula. The at. reflection in a body whose atoms are not organized into a crystalline structure

resembles the scattering of light by a fog. The at. reflection from a crystal furnishes a diffraction spectra analogous to that of light when a sufficiently fine atomic lattice, such as that furnished by the atoms of a crystal, is used as a grating. The *diffraction of X-rays* was not successfully accomplished until M. von Laue had shown that the difficulties arising from the extreme shortness of the wave-length could be overcome by utilizing the regular grouping of the atoms in a crystal as a kind of diffraction grating—*vide* **1.** 11, ·8. As a result, X-ray spectra, using anti-cathodes of the different elements, have been obtained. The phenomena have been employed in investigation on the minute structure of crystals. H. G. J. Moseley photographed the X-ray spectra of different elements. With the lighter elements emitting strong *K*-radiations, the wave-length decreases as the at. wt. diminishes; and the spectrum contains at least two lines of which the line of longer wave-length called the α-line is the more intense; the β-line comes next in order of intensity. H. G. J. Moseley's results are indicated in Table V. The *L*-radiations, Table V, give spectra made up of at least five lines—α, β, γ, δ, ϵ—reckoned in order of decreasing wave-length and decreasing intensity. The α-line in the *K*-spectrum is really a doublet; and there are a number of other fainter lines in both the *K*- and *L*-series of spectra. This is illustrated by Fig. 12.

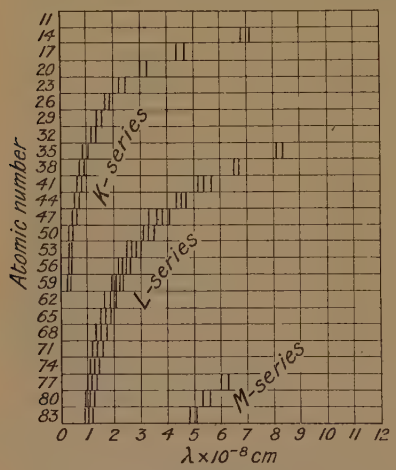

FIG. 12.—X-ray Spectra of some Elements.

TABLE V.—WAVE-LENGTHS OF THE TWO PRINCIPAL LINES IN THE X-RAY SPECTRA OF THE ELEMENTS.

	K-series.						*L*-series.				
	λ×10⁸ cm.			λ×10⁸ cm.			λ×10⁸ cm.			λ×10⁸ cm.	
	α	β		α	β		α	β		α	β
Al	8·364	7·912	Cu	1·549	1·402	Zr	9·091	—	Nd	2·382	2·175
Si	7·142	6·729	Zn	1·445	1·306	Nb	5·749	5·507	Sa	2·208	2·008
Cl	4·750	—	Y	0·838	—	Mo	5·423	5·187	Eu	2·130	1·925
K	3·759	3·463	Zr	0·794	—	Ru	4·861	4·660	Gd	2·057	1·853
Ca	3·368	3·094	Nb	0·750	—	Rh	4·622	—	Ds	1·914	1·711
Ti	2·758	2·524	Mo	0·721	—	Pd	4·385	4·168	Er	1·790	1·591
V	2·519	2·297	Ru	0·638	—	Ag	4·170	—	Ta	1·525	1·330
Cr	2·301	2·093	Pd	0·584	—	Sn	3·619	—	W	1·486	—
Mn	2·111	1·818	Ag	0·560	—	Sb	3·458	3·245	Os	1·397	1·201
Fe	1·946	1·765	Sn	0·50	0·43	La	2·676	2·471	Ir	1·354	1·155
Co	1·798	1·629	Sb	0·48	0·41	Ce	2·567	2·360	Pt	1·316	1·121
Ni	1·662	1·506	W	0·203	0·177	Pr	2·471	2·265	Au	1·287	1·092

H. G. J. Moseley further showed that when the increase in the at. wt. of the element is plotted with the logarithm of the corresponding decrease in wave-length, the curve does not run smoothly; but if the square roots of the vibration frequencies be plotted against a series of natural numbers, the curve runs almost smoothly. The numbers, called **atomic numbers,** represent very closely the order of the elements in the periodic table. The at. number is nearly half the at. wt. At. numbers are not mere integers, but represent a fundamental property of the atoms, because if at. wt. are employed in place of at. numbers, the relationships shown in Fig. 13

are not nearly so satisfactory. Similarly also with several other physical properties. It is, however, putting the blind eye to the telescope to pretend that the substitution removes the anomalies in the periodic classification on the chemical side emphasized **1, 6, . . .** That Chapter remains unaffected by the substitution. M. Duvallier has discussed this subject.

The wave-length of the X-ray is inversely proportional to $(N-a)^2$, where N is the at. number, and a is a constant; or the frequency or $\nu=b(N-a)^2$, where a and b are constants. Fig. 13 shows the results for the K- and L-radiations. No known element is left unprovided in the scheme, and the harmony in the relationship justifies the assumption that certain blanks may be regarded as representing yet undiscovered elements. In the range from hydrogen to gold there are blanks for three new elements—one between molybdenum and ruthenium; another between lutecium and tantalum; and one between tungsten and osmium. The order of the atomic numbers is that of the at. wt. except in the cases of argon, cobalt, and tellurium. H. G. J. Moseley's work has been extended by M. Siegbahn and E. Friman, and W. Stenström, and the K-series has been followed down to sodium, and the L-series down to zinc and up to uranium.

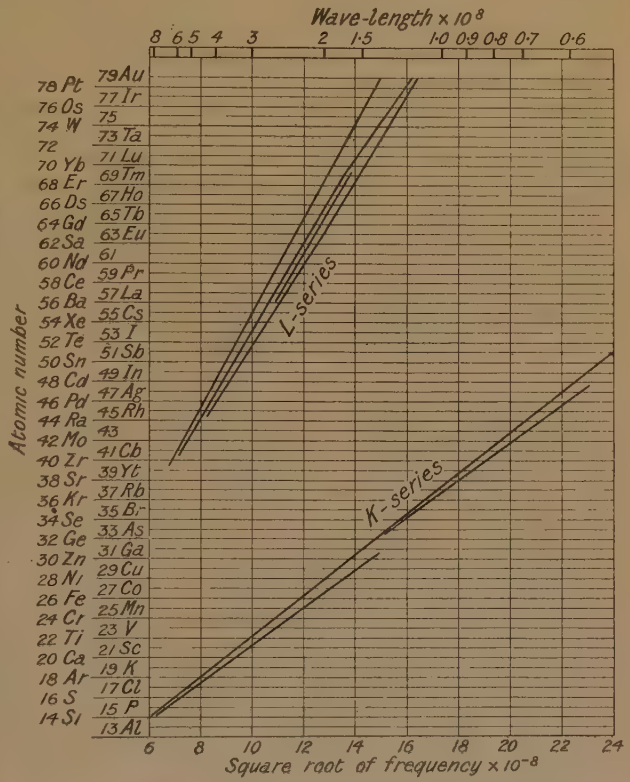
Wave-length × 10⁸
8 6·5 4 3 2 1·5 1·0 0·9 0·8 0·7 0·6
Atomic number
78 Pt 79 Au
76 Os 77 Ir
74 W 75
72 73 Ta
70 Yb 71 Lu
68 Er 69 Tm
66 Dy 67 Ho
64 Gd 65 Tb
62 Sa 63 Eu
60 Nd 61
58 Ce 59 Pr
56 Ba 57 La
54 Xe 55 Cs
52 Te 53 I
50 Sn 51 Sb
48 Cd 49 In
46 Pd 47 Ag
44 Ra 45 Rh
42 Mo 43
40 Zr 41 Cb
38 Sr 39 Yt
36 Kr 37 Rb
34 Se 35 Br
32 Ge 33 As
30 Zn 31 Ga
28 Ni 29 Cu
26 Fe 27 Co
24 Cr 25 Mn
22 Ti 23 V
20 Ca 21 Sc
18 Ar 19 K
16 S 17 Cl
14 Si 15 P
13 Al
L-series
K-series
6 8 10 12 14 16 18 20 22 24
Square root of frequency × 10⁻⁸

FIG. 13.—Moseley's Relation between the Atomic Number and Frequency of K- and L-radiations.

The relation between the vibration frequency and the at. number has been discussed by G. A. Anslow and co-workers; H. E. Ives and O. Stuhlmann, C. Runge and H. Precht, H. Bell, H. S. Allen, and W. Kossel, G. le Bas, R. Ledoux-Lebard and A. Dauvillier, T. E. van Auren, G. A. Anslow, W. Duane, etc. L. Vegard inferred that since it is possible to predict some X-ray frequencies as functions of the at. wt., the atom contains plane rings of electrons; but A. Smekal denies this. The relation between the at. wt. and the at. number was discussed by R. G. Durrant, and W. D. Harkins and E. D. Wilson. The relation between the L-series of spectra and at. wt. was developed by F. Kirchhof.

The order of the at. numbers is the same as the order of the at. wt. except where the latter disagrees with the order of the chemical properties so that the at. number in the periodic table is a more fundamental index of quality than the at. wt. **The wave-length, or the vibration frequency, of the characteristic X-rays from different elements changes from element to element by regular jumps.** The steady decrease in the wave-length of the characteristic X-rays of a series of elements in the periodic table depends on some fundamental property of the atoms. As pointed

out by W. Kossel, the continuity of the *K*-line spectra of the different elements from the lowest to the highest at. number, shows that the periodicity observed in the outer valency electrons does not extend to the innermost electrons. As an hypothesis, it has been suggested that the increments are due to the successive addition of a unit electric charge to the nucleus of the atom ; and that the magnitude of the nucleus of an atom is proportional to a number—the at. number—indicating the place of the element in the periodic table—hydrogen has a nucleus charge of one unit, helium two, etc. This shows that the wave-length of a characteristic radiation depends entirely on the magnitude of the nuclear charge of the atom which in turn depends on the at. number. J. Chadwick found that the nuclear charge of a platinum atom is 77·4, the at. number is 78 ; while the nuclear charges of silver and copper atoms are 46·3 and 29·3, when the at. numbers are respectively 47 and 29. The same at. number may be borne by several elements with different at. wt., and in the case of radioactive substances, with different stabilities. These elements may be inseparable by the ordinary chemical or physical tests. These elements are the isotopes of F. Soddy ; and they presumably have in common the same nuclear charge. The isotopes might also be expected to yield the same X-ray spectrum. E. Rutherford and E. N. da C. Andrade found the spectrum of the soft rays from radium-*B*, is identical with the *L*-radiation of lead.

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§ 7. The Photoelectric Effect

According to the quantum theory of energy—*vide* **1**. 13, 15—the intensity of the disturbance produced by the appropriate type of incident light must exceed a certain limiting value before any light can be emitted ; it is impossible for a radiator to emit any energy when the supply of energy is less than one quantum. J. Franck and G. Hertz [1] bombarded a rarefied mercury vapour with cathode rays, so arranged that the electrons had a definite and determinable velocity dependent upon the difference of potential between the electrodes. So long as the difference of potential was less than 4·9 volts, the emitted light gave an ill-defined continuous spectrum, but at 4·9 volts, a single bright line appeared of wave-length 2536·72A. Calculations show that at the critical moment when the light appears, the energy of the negative particles constituting these rays is equal to that required by the quantum theory, namely $h\nu$, where h is M. Planck's constant $6{\cdot}62 \times 10^{-27}$ erg. sec., and ν is the vibration frequency, *i.e.* ν=39410. When the voltage reaches 6·7, a band of wave-length 1849·6, or vibration frequency 54066, appears ; and with the voltage 10·4, other lines appear ; but, according to J. C. McLennan, the lines 1849·6 and 2536·72 did not appear. H. L. Dodge describes the following qualitative experiment in further illustration of the hypothesis that definite units of energy are required to produce light of any specified wave-length :

An exhausted bulb, containing a trace of gas, is placed near a coil traversed by a rapidly alternating current. The bulb becomes the secondary of a transformer, and the tendency is for currents to be set up in the gas. If the bulb is placed close to the coil it experiences a strong field, while if it is withdrawn a little the field is weakened. If the bulb is more

than a certain distance away, the light given out is diffused throughout the whole tube; but on the critical limit being passed, a brilliant ring of light springs into being inside the bulb. The ring disappears just as abruptly as the distance is again increased, being in all cases either exceedingly bright or entirely absent. The spectrum of the light from such a bulb also changes abruptly with the appearance and disappearance of the ring. The same general effect is produced with different gases, but the spectrum and the strength of the field at which the ring appears are different for each gas and characteristic of the gas. It is also found that the absorption of energy changes abruptly with the appearance of the ring, at which time the conductivity of the gas suddenly increases, resulting in a larger current and a corresponding increase in the absorption of energy.

The photoelectric effect—described **2.** 18, 5—whereby a surface illuminated by ultra-violet light becomes positively charged and facilitates the passage of electricity in such a direction as to charge the surface positively, is explained as being due to the emission of electrons. P. Lenard discovered the remarkable fact that the maximum velocity of the emitted electrons does not depend on the intensity of the illumination no matter whether this intensity is varied by altering the distance of the source of illumination, or by introducing absorbing screens. Rather does the velocity of the ejected electrons depend on the vibration frequency of the incident light. The number of electrons emitted per sec. per unit area, increases with the intensity of the incident monochromatic light. The phenomena are discussed in H. S. Allen's *Photoelectricity* (London, 1913), and in A. L. Hughes' *Photoelectricity* (Cambridge, 1914). Let V denote the velocity of the emitted electron, and m its mass; let W denote the work required to get the electron through the surface of the metal, *i.e.* the latent heat of evaporation of the electrons per electron, at absolute zero of temp. The energy required for the expulsion of the electron comes from the incident light, and on the basis of M. Planck's quantum theory, this must be equal to $h\nu$. The kinetic energy of the electron is $\frac{1}{2}mV^2$, hence

$$h\nu = W + \tfrac{1}{2}mV^2$$

If P denotes the difference of potential through which the electrons must pass in order to acquire the velocity V, and e the electric charge on an electron, $4{\cdot}774 \times 10^{-10}$ electrostatic units, the relation between kinetic energy of the electron as it leaves the metal is equal to the product of the charge, e, by the potential P, or $Pe = \frac{1}{2}mV^2$;

$$\mathrm{P} = \frac{h\nu}{e} - \frac{W}{e}$$

This relation can be tested experimentally. The value of W can be obtained from thermoelectric data combined with the temp. variation of the rate of emission of electrons when the metal is heated. For platinum, F. Deininger obtained $W = 5{\cdot}03$ volts; H. A. Wilson, 5·39 volts; and O. W. Richardson, 5·61 volts—average, 5·34 volts or $8{\cdot}32 \times 10^{-12}$ ergs. A. L. Hughes measured the relation between W and ν. The values of P and the corresponding frequencies have been measured by O. W. Richardson and K. T. Compton, and others. R. A. Millikan measured the minimum positive potential necessary to be applied to the illuminated surface in order to prevent the emission of electrons. The observed value h/e is within five per cent. of that calculated in other ways; and the general results confirm the quantum theory of radiation. The tube-of-force or æther-string theory does not explain the phenomena.

The relation between photochemical reactions and A. Einstein's theory has been previously discussed—*vide* **2.** 18, 5. J. Plotnikoff has shown that on calculating the energy absorbed by one mol, from light of various wave-lengths, the extreme ultra-violet, $100\mu\mu$, gives up 300,000 cals. and X-rays 3×10^9 cals., which indicates that with decreasing wave-length light becomes much more active, until with X-rays, all mols. will be simply destroyed. Further, all atoms in all reactions in all solvents must react with the same velocity at all temp., and must take up the same quantity of energy. A number of other photochemical reactions deviate 9 to 22 per cent. from Einstein's law, and this is taken to show that

this law in its present form cannot be maintained. With the photolyses of hydrogen iodide and bromide the law is in approximate agreement with facts since the divergence varies only between −3·3 and 4·0 per cent. G. Kornfeld showed that in the case of hydrogen dioxide, the law fails because the decomposition is not a primary light effect.

The ejection of electrons from solids bombarded by X-rays may be regarded as a kind of photochemical effect, for here the velocity of the emitted electrons is proportional to the difference of potential between the electrodes of the tube producing the rays. The harder the X-rays, the greater the velocity of the emitted electrons. Assuming that the X-rays transfer a quantum of energy from an electron bombarding the anode of the X-ray tube to the surface on which the X-ray impinges, then, since $Pe=h\nu$, and $\nu=V_\infty/\lambda$, where V_∞ denotes the velocity of light, 3×10^{10} cms. per sec., and λ denotes the wave-length of the X-ray, $Pe=hV_\infty/\lambda$. With a voltage $P=40{,}000$, *i.e.* $40{,}000\div300$ electrostatic units, it follows, on substituting the values indicated above for h, V_∞, e, and P, that $\lambda=3\times10^{-9}$ cms.—a result in agreement with that obtained in other ways.

Besides the *normal photoelectric effect*, on which the number of electrons liberated by light of a given intensity and frequency depends only on the amount of light absorbed by the metal, there is the *selective photoelectric effect*, exhibited by the alkali metals, in which this number is a maximum for some particular frequency of light, and is less for frequencies either greater or smaller. The frequency at which the maximum emission occurs is characteristic of the exposed metal surface, and decreases with decreasing at. wt. Similarly, too, with the X-rays, with a certain definite voltage in the exciting tube, there occurs an abnormal emission of electrons from the surface exposed to the X-rays, and the frequency of the X-rays required to produce this abnormal emission is nearly proportional to the at. wt. of the exposed metal. O. J. Lodge discussed the critical velocity, critical frequency, and critical distance of electrons at the moment of their liberation from molecules stimulated by light.

Isaac Newton's corpuscular theory of light was abandoned in favour of the æther-wave theory. The former failed to explain interference phenomena; electromagnetic waves; and phenomena associated with the velocity of light. A. Einstein's equation is based on a kind of corpuscular theory of light. The equation explains phenomena which do not fit the æther wave-theory so well. Nevertheless, added R. A. Millikan:

> The physical theory of which A. Einstein's equation was designed to be the symbolic expression, is so untenable that A. Einstein himself no longer holds to it, and we are in the position of having built a very perfect structure, and then knocked out entirely the underpinning without causing the building to fall. It stands complete and apparently well tested, but without any visible means of support. These supports must obviously exist, and the most fascinating problem of modern physics is to find them. . . . The atomic and electronic worlds have revealed themselves with beautiful definiteness and wonderful distinctness, but their relation to the world of æther waves is still a profound mystery.

C. Ramsauer devised a test to find if the existence of energy in definite quanta in the form of trains of light waves, gives rise to the quantum emission of photoelectrons. He concluded that the quantum-like behaviour of photochemical processes must be the result of the mechanical processes of absorption of the light energy taking place in the atom, and is certainly not caused by single light-quanta present in the wave-trains of the light as definite entities. C. F. Bickerdike discussed the relation between radiation electrons and the æther.

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§ 8. The Radiation Theory of Chemical Action

The speed of chemical reactions varies with the conc. of the reacting molecules; in the simple case of a unimolecular reaction commencing with a mols of material, the amount of substance dx which disappears in the time dt is equal to the conc. x at the time t, when x of a has been transformed. Consequently, $dx/dt=-k(a-x)$, where k is the so-called velocity constant. Otherwise expressed, $x=a(1-ex^{-kt})$. This is the expression, in mathematical language, of L. Wilhelmy's law that the speed of chemical action is proportional to the amount of substance taking part in the reaction. Why do not all molecules undergo change at one time? What regulates the speed of the reaction in such a way that only a certain fraction of the total number of molecules changes in unit time? If all the molecules were in the same condition, then either no chemical change would take place at all, or else all the molecules would undergo transformation at the same instant.

According to the kinetic theory, a certain number of molecules, at any given instant, possess a much greater, and others a much smaller, velocity of translation than the average. J. W. Mellor [1] assumed that the kinetic energy of translatory motion may be converted into energy of atomic vibrations; when the latter exceeds a certain limiting value, the atoms take up a more stable configuration. The rate of chemical action then depends on the rate at which the velocities of the molecules are accelerated beyond the limiting value. S. Arrhenius represented the effect of temp., $T°$ K., on the velocity constant k, by $d \log k/dt=AT^{-2}$; and he showed that a rise of 10° may cause the velocity of a reaction to be augmented 200 to 300 per cent. under conditions where the collision frequency of the molecule is only 2 per cent. It is therefore certain that the effect of a rise of temp. on these reactions is not to be explained as the effect of an accelerated speed of molecular motion, but rather as inducing a change in the internal energy of the molecules. It has generally been assumed that the molecules are activated in some way before they react, and that this activation is the one affected by temp. A in S. Arrhenius' equation is half the energy required to change a mol of the assumed inactive modification to the active form. This leads to the effect of catalysts. S. Arrhenius predicted that the temp. coeff. should be diminished in a homogeneous system by increasing the conc. of the catalyst. W. C. McC. Lewis found the temp. coeff. of the speed of hydrolysis of methyl acetate is independent of the conc. of the acid. H. S. Taylor also doubted the existence of activated molecules. According to E. Marcelin, when the internal energy of a molecule reaches or exceeds a certain critical value, the molecule is capable of reacting chemically. The additional energy which a molecule in the mean or average state must receive in order to make it reactive, can be called the *critical increment*. On these assumptions, he deduced a formula resembling that of S. Arrhenius' $d \log k/dT=E/RT^2$, where E represents the critical energy that must be absorbed by a molecule to render it active. J. Rice developed the relation $d \log k/dT=(V_c-V_m+\frac{1}{2}RT)/RT^2$, where V_m is the mean value of the potential energy of the molecule, V_c is the critical value it must attain before chemical action can occur. R. C. Tolman has also studied the kinetics of the radiation theory of chemical action. N. R. Dhar argues that the general experience that reactions with the largest temp. coeff. are also most sensitive to light, fits the radiation hypothesis. From observations on the effect of ultra-violet light the absorption spectra, E. C. C. Baly assumed that in the process of activation the bonds between the atoms or atomic groupings are loosened.

J. Perrin, and W. C. McC. Lewis have assumed that *energy of the radiation type is the ultimate source of all the energy which makes chemical reactions possible; every chemical reaction is produced by radiations having a specific wave-length.* With reactions which proceed at ordinary temp. it is assumed that short infra-red radiation is effective, and such is necessarily present throughout a material system in virtue of its temp., for the temp. of a substance is directly due to radiation which is being continually absorbed and emitted by the constituent molecules. Only at absolute zero will such radiation be absent. The effective radiation with reactions which proceed only at high temp. presumably belong to the visible or ultra-violet region. The assumption that radiation is the *fons et origo* of all reactions which occur at ordinary temp. is different, though similar to that involved in the so-called photochemical reactions discussed in **2.** 18, 5. In photochemical reactions, the energy applied is usually largely in excess of the net energy involved in the reaction, whereas with the infra-red absorption the energy increment is not a large fraction of the chemical energy of the reaction. According to G. N. Lewis, in each molecule there are two sets of charged particles capable of acting as oscillators, (i) the positively charged nuclei and (ii) the electron. On account of the relatively high mass of the positive particles, it seems probable that they are never, or almost never, capable of vibrating with a frequency sufficiently high to come within the scope of the visible spectrum, but they rather cause absorption in the ultra-red. On the other hand, those light and indeed almost massless particles called electrons are usually held lightly enough, so that their natural period is well above that of the visible spectrum, and they can therefore absorb in the ultra-violet region. Thus, in the great majority of chemical compounds which are colourless, the positive parts have too low a frequency and the negative parts too high a frequency to affect the visible spectrum. If, however, the constraints under which the electrons are held are in some way loosened, their frequency of vibration will diminish, and then ultimately they may become so loosely held as to absorb in the visible spectrum.

W. C. McC. Lewis has developed the hypothesis that *the rate at which a substance decomposes or interacts depends not only on its concentration, but simultaneously upon the density of that type of radiation which the substance can absorb;* and he has applied Einstein's theory of radiation. The critical increment of a molecule is one quantum of absorbable radiant energy; and A. Einstein's law of photochemical equivalency, then enables the effect of temp. on the velocity constant to be calculated; and conversely, from the observed effect of temp. on the velocity of a reaction it is possible to compute a value for the wave-length of the radiation which a substance is capable of absorbing and by means of which the reaction is activated. The hypothesis also enables the heat of the reaction to be calculated. He calculated the energy increment from R. Marcelin's formula which in the hydrolysis of methyl acetate at 25° and 35°, assumes the form $\log k_{35} - \log k_{25} = E/R(\frac{1}{298} - \frac{1}{308})$. This gives $E = 16{,}800$ cals. per mol, or $1{\cdot}03 \times 10^{-12}$ ergs per molecule. From Einstein's law, and W. W. Coblentz's value $\lambda = 7{\cdot}5\mu$ for the infra-red radiation of methyl acetate, $h\nu = 0{\cdot}262 \times 10^{-12}$ ergs, and therefore $4h\nu$ should supply the required energy. He also showed from the probable free-path and the electrolytic velocity of the H·-ion, that it would have a vibration frequency falling in the region of the known absorption.

W. C. McC. Lewis' hypothesis is in conformity with M. Trautz's work and with that of H. Krüger, who explained the process of soln., soln. press., solubility, and ionization on the basis of radiation; and showed that the last is related with the dielectric constant of the solvent. The velocity constant of a reaction depends on the cube of the index of refraction of the system for the wave-length of the absorbed radiations which cause the chemical change. There is a close relation between the refractive index and the dielectric capacity of a medium; hence also there is a close relation between the dielectric capacity of the medium in which the reaction proceeds. The function of a catalyst, said W. C. McC. Lewis, is to absorb

infra-red radiations and transfer their energy to the reacting molecules. Catalysis is thus a special case of a chemical reaction where the absorption is effected largely by the catalyst instead of by the reacting substance. Reactions taking place in soln. are regarded as catalytic. This, however, is doubtful. With uncatalyzed homogeneous bimolecular gas reactions, like $2HI=H_2+I_2$, the agreement with theory is satisfactory, for in that case the index of refraction is nearly unity in conformity with Einstein's law. In heterogeneous catalytic reactions, the energy increment is lowered at the contact surface, as indicated in I. Langmuir's hypothesis of the distribution of the molecules and atoms at the interface between two surfaces. In the case of unimolecular reactions, like the dissociation of phosphine, the agreement with theory is very poor, for the observed velocity constant is 10^7 times greater than that calculated from Einstein's law on the assumption that absorption is continuous or discontinuous. S. Dushman and E. K. Rideal found an equation of the type $dN/dt=\nu e^{-h\nu/kt}$ to give good results with phosphine; here N is the number of molecules reacting per second; ν is the vibration frequency; and the other symbols have their usual signification. W. E. Garner believes the agreement rather due to chance than to compatibility of hypothesis.

E. C. C. Baly developed a theory of spectroscopic and fluorescent phenomena on the assumption that a molecule may absorb radiation by quanta of a given frequency, and as a result of chemical action it may radiate a larger number of quanta of lower frequency. He explained the thermal decomposition of phosphine, the photochemical decomposition of hydrogen peroxide, and the hydrolysis of acetone where chemical action is in excess of that calculated from Einstein's theory, by assuming that this internal radiation is re-absorbed, resulting in further chemical action. W. T. David showed that there is an infra-red radiation, $\lambda=2{\cdot}8\mu$ and $4{\cdot}4\mu$, during the explosive combination of oxygen with coal gas or hydrogen. The temp. of the reaction is 1200°, but it is assumed that the radiation is due to chemical action, and is not a temp. effect.

F. Daniels and E. H. Johnston's work on the thermal and actinic decomposition of gaseous nitrogen pentoxide which is unimolecular at room temp. showed that the critical increment is 24,700 cals., and it follows that the reaction should be catalyzed by light of wave-length $\lambda=1{\cdot}16\mu$. This is not confirmed by observation. The reaction is accelerated by light of wave-length $\lambda=400$–$460\mu\mu$, but only in the presence of nitrogen peroxide. It is suggested that the catalytic effect of nitrogen peroxide is due to its absorption of blue light over a wide spectral range, and through fluorescence, radiation is emitted in the infra-red region, where its absorption lines coincide with those of nitrogen pentoxide, causing the decomposition of the latter. This hypothesis has not been checked by observation.

If radiations of specific wave-length are alone effective in producing chemical reactions, it is a waste of energy to invoke the entire spectrum of radiations to produce a reaction dependent on temp. One fraction of the radiations may produce the desired reaction, and other fraction may produce a reverse reaction and so cancel the effect of the first. It therefore follows, as P. Weiss has shown, that instead of this crude method of activating chemical reactions, the more elegant and efficient procedure will involve a selection of the specific radiations required to produce the given effect.

I. Langmuir concluded that the radiation theory of chemical action is invalid because (i) it has not satisfactorily demonstrated that the radiation emitted by a chemical reaction, as calculated from the temp. coeff., falls in the absorption region of the system, for, in the case of hydrogen and certain colourless gases, there are no absorption bands at the frequencies predicted by the hypothesis; and (ii), as M. Polanyi has shown, the hypothesis is untenable because the total radiation is not nearly sufficient to account for chemical activation. The energy required for the unimolecular decomposition of phosphine is much greater than that calculated by the radiation laws as being supplied through the walls of the containing vessel at the calculated frequency. The laws which govern the temp. coeff. of a reaction

and the emission of monochromatic radiation are similar because they are both expressions of probabilities. A unimolecular reaction is independent of molecular collision because the time between collision is very great compared with the time of activity. The energy of activation cannot come from molecular collision, or from radiant energy emitted by the walls, but it must come from the latent internal energy of the molecule. Hence, said I. Langmuir, the internal energy of the molecule is the ultimate source of its activation. F. A. Lindemann also claimed that, according to the radiation theory, many reactions should be photosensitive which fail to exhibit the effect—for example, the inversion of sucrose is not affected by sunlight. W. C. McC. Lewis argued that the null effect of sunlight is due to the screening effect of a layer of the soln. T. W. J. Taylor tested the hypothesis with soln. of sucrose where the screening effect was eliminated and obtained a negative result. The objections have been discussed by W. C. McC. Lewis and A. McKeown. M. Polanyi tried to show that the quantum hypothesis is invalid when applied to chemical processes.

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§ 9. Positive or Canal Rays

The corpuscular theory of the positive rays has no other justification than that it explains our present-day knowledge of the phenomenon in the simplest possible way.—E. GEHRCKE.

When a perforated cathode is employed in the vacuum tube for producing cathode rays, E. Goldstein [1] first noticed that streams of violet light passed through the perforations or canals and emerged behind the cathode on the side remote from the anode, and hence he called these streams *Kanalstrahlen* (canal rays). In the apparatus illustrated in Fig. 14, the canal rays travelling towards the right strike against a plate *b* connected with an electroscope *B*, and there show a positive charge; the cathode rays travelling towards the left impinge on the plate *a* connected with an electroscope *A*, and there show a negative charge. The canal rays have been investigated by methods similar to those employed for the cathode rays. W. Wien,

P. Ewers, and P. Villard have shown that the canal rays are streams of particles the majority of which are positively electrified—hence, the term **positive rays** is replacing the older term **canal rays.** The streaming particles travel in straight lines and produce a phosphorescence (usually violet) when they impinge upon glass, etc. A. Wehnelt showed that the positive rays of oxygen oxidize copper, but G. C. Schmidt found that the oxidation is not directly due to the impact of the rays, but is an indirect effect due to the production of active oxygen as the rays pass through the gas; positive rays in hydrogen gas exert a reducing action. H. P. Waran discussed the "sand-blast" action of the rays on glass. The theory of the canal rays has been discussed by G. Huch, A. Ruttenauer, G. Mie, etc.

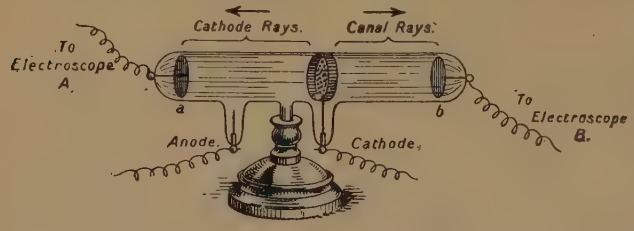

FIG. 14.—Tube for Canal or Positive rays.

H. Baerwald, V. F. Hess and M. Hornyak, and J. Stark have discussed ionization by canal rays. The speed of the positive electrons is usually less than that of the negative electrons; and they are not so sensitive to magnetic influences. Measurements similar to those employed for the cathode rays show that the positively charged particles must be of the atomic dimensions, and in no case is the mass of the positive ion perceptibly less than that of the hydrogen atom. W. Wein found for air, a velocity $V=3{\cdot}6\times10^7$ cms. per sec., and for the ratio e/m, $3{\cdot}2\times10^3$; E. Gehrcke and O. Reichenheim, for lithium, $V=2{\cdot}7\times10^7$ cms. per sec., and $e/m=1{\cdot}15\times10^3$; for sodium, $V=1{\cdot}8\times10^7$ cms. per sec., and $e/m=0{\cdot}41\times10^3$; and for strontium, $V=1{\cdot}1\times10^7$ cms. per sec., and $e/m=0{\cdot}21\times10^3$. For electrolytic hydrogen, $e/m=9{\cdot}5\times10^3$. Hence, the ratio

$$\frac{m_{Li}}{m_H}=8{\cdot}3\,;\quad \frac{m_{Na}}{m_H}=23\,;\quad \frac{m_{Sr}}{m_H}=90$$

showing that the masses of the positive ions are nearly equal to their at. wt. J. J. Thomson, W. Hammer, etc., have also evaluated the ratio e/m for these rays. Remembering that, so far as we can tell, all electrons are the same, and have a mass 1840 times less than that of the hydrogen atom, while the mass of the positively charged particles depends upon the nature of the gas, and is virtually the same as that of the atom from which it is derived, it is probable that **when a gas is ionized, one or more negatively electrified particles—electrons—are expelled from the atom, and the corresponding positively charged nucleus remains.**

E. Goldstein said that the spectrum of the positive rays is the same as the spectrum of the gas in the discharge tube. J. Stark found that the spectral lines of the positive rays in hydrogen are displaced towards the violet end when the rays are observed moving towards the spectroscope; and towards the red end when the rays are receding from the spectroscope. J. Stark, W. Hermann and S. Kinoshita, obtained similar results with nitrogen and mercury; J. Stark and K. Siegl, with sodium and potassium vapours; K. Siegl, F. Paschen, and J. Stark, with oxygen; J. Stark, with aluminium; S. Kinoshita, with carbon; H. Rau, and E. Dorn, with helium; and E. Dorn, with argon. H. Wilsar, J. Stark and W. Hermann, and G. S. Fulcher studied the spectra of the positive rays. The spectra obtained when the positive rays strike alkali salts show the characteristic lines of the metal, and these lines are more readily excited in the salts than in the metals themselves. The subject has been studied by V. Carlheim-Gyllensköld, and J. Stark and G. Wendt. The results by the latter are indicated in Table VI, and the last column shows the critical energy which is required to develop the spectrum of the metal.

TABLE VI.—THE EFFECT OF POSITIVE RAYS ON DIFFERENT COMPOUNDS.

Salt.	Light.		Critical energy in volts.
	Colour.	Wave-length λ.	
Lithium chloride	red	—	600
Lithium oxide	red	6710	600
Sodium chloride	yellow	—	750
Potassium chloride and oxide	—	580	<2400
Rubidium suboxide	—	572	<3500
Cæsium chloride	—	566	<4500
Magnesium chloride	—	518	<1200
Calcium fluoride	reddish-violet	—	1150
Calcium carbonate	,,	—	1500
Calcium sulphate	,,	—	1500
Calcium oxide	,,	—	1400
Strontium chloride	—	496	<2500
Barium chloride	—	554–493	<2500
Thallium sulphate	—	535	4500
Zinc oxide	—	475	<4600
Aluminium oxide	—	396	<4500

If a mixture of different kinds of electrified particles travelling at a high velocity in one thin stream be passed simultaneously through electric and magnetic fields disposed at right angles to one another, the different kinds of particles are sorted into a number of smaller separate streams. The various streams can be demonstrated by causing them to impinge upon a fluorescent screen of, say, willemite, or on suitable photographic plates.

An idea of the apparatus employed can be obtained from Fig. 15. *A* represents the discharge tube, about 30 cms. in diameter, containing the gas under a low press. The anode is placed in a side tube, and the cathode *C* is placed in the neck of the flask. The cathode is an aluminium rod pierced with a narrow copper tube about 8 cms. long, and less than $\frac{1}{10}$th cm. in diameter. To protect the tube from stray magnetic fields which might cause the particles to impinge on the walls of the tube and so be lost, the copper tube is enclosed for most of its length in a thick iron tube, and iron screens *VW* protect the main discharge from the influence of the magnet. To cool the various wax joints they are surrounded with a water-jacket *J*, this prevents the wax being melted when the cathode becomes hot. The rays pass between *LM*, which consists of two soft-iron blocks which are continuations with the pole pieces *PQ* of an electromagnet, from which they are electrically insulated by mica plates. This insulation enables the soft-iron blocks *LM* to be charged electrostatically. In this way, the positive particles are simultaneously subjected to conterminous electric and magnetic fields. After passing these fields, the rays pass into *F* and fall either on a photographic plate or a glass plate covered with powdered willemite. F. W. Aston has introduced many improvements conducing to greater precision.

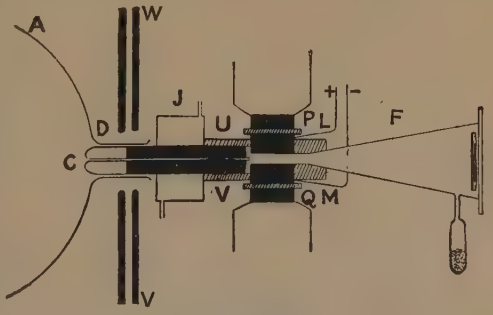

FIG. 15.—J. J. Thomson's Positive Ray Apparatus.

When the positive rays pass the electric and magnetic field they will be acted upon by forces *Xe* and *He*, where *X* denotes the strength of the electric field and *H* that of the magnetic field; *e* denotes the charge on each particle, and *v* their velocity. These forces cause the particle which strikes the photographic plate to be deflected through a distance $k\,He/mv$ in the case of the magnetic field, and k_2Xe/mv^2 in the case of the electric field—*m* denotes the mass of the particle, and k_1 and k_2 are constants dependent on the dimensions of the apparatus. The fields are so disposed that the two deflections are at right angles to one another. *O*, Fig. 16, represents the position on the plate when the undeflected ray will

strike; OX and OY respectively denote the directions of the electric and magnetic deflections which deflect the particle to some point, say P. Then

$$\text{Electric deflection } PK = x = k_2 \frac{Xe}{mv^2}; \quad \text{Magnetic deflection} = PJ = y = \frac{He}{mv}$$

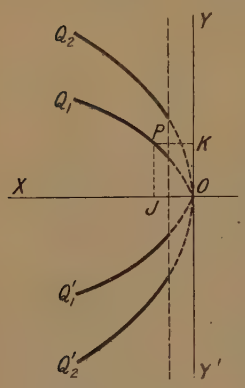

FIG. 16.

so that

$$\frac{y}{x} = \left(\frac{k_1 H}{k_2 X}\right) v; \quad \frac{y^2}{x} = \left(\frac{k^2 H^2}{k_2 X}\right) \frac{m}{e}$$

If the strengths of the two fields are kept constant, the quantities in brackets are also constant, and y/x will measure the velocity, and y^2/x, the ratio of the mass to the charge. If all the particles were identical and had the same velocity, the spot O would be shifted to P; but the velocities of the particles are not all the same; and the rays are therefore drawn out into a line or band OPQ; and all the particles for which m/e is constant will lie on the same parabolic curve $y^2 = ax$. If the particles have different at. masses, they will be sorted out into a series of parabolas OQ_1, OQ_2, . . . Since the velocity y/x cannot exceed a certain limiting value, these curves will stop short at some definite distance from the OY axis. The curves can be measured and y/x and y^2/x evaluated. If the field is reversed during the exposure, the deflections are reversed, and symmetrical parabolic curves OQ'_1, OQ'_2, . . . are produced in the XOY′ quadrant.

J. J. Thomson calls the series of small streams obtained from the original stream, the **electric spectrum of the atoms,** for the stream of electrified atoms is separated by this treatment into sub-streams—much as a beam of light from an illuminating gas is analyzed into different rays by passing through the prism of a spectroscope. From the displacement of the path of the stream of electrified particles under the influence of electric and magnetic forces of known intensity, J. J. Thomson has developed what he calls **positive-ray analysis;** this furnishes evidence on such subjects as:

Are the atoms of an element all alike?—The particles in any one stream are presumably all of the same kind because the parabolic curves are sharply divided, and show no tendency to merge one into another. If it were otherwise the curves would be "fuzzy." Ordinary chemical analysis cannot decide whether particles of one kind of substance have all the same mass, because it can deal only with the average masses of billions of particles. J. J. Thomson found unknown lines indicating that the gas which has been called **neon** is probably a mixture of two different gases of at. wt. 20 and 22—but with a preponderating amount of the former. F. W. Aston, and A. G. Dempster have followed up J. J. Thomson's positive ray method of analysis, and found that many elements can be resolved into two or more isotopic forms, which have so nearly the same at. wt., and so similar properties that they cannot be separated by known processes.

Hydrogen, helium, nitrogen, oxygen, carbon, sodium, arsenic, phosphorus, and *fluorine* do not show any isotopic forms; *boron* (10 and 11), *lithium* (6 and 7), *potassium* (39 and 41), *cæsium* (85 and 87), *neon* (20 and 22), *argon* (36 and 40), *sulphur* (32 and ?), *chlorine* (35 and 37), and *bromine* (79 and 81) have two isotopic forms with the respective at. wt. indicated in brackets; *magnesium* (24, 25, and 26); and *silicon* (28, 29, and possibly 30) have three isotopic forms; *krypton* has six isotopic forms with at. wt. 78, 80, 82, 83, 84, and 86; while *xenon* and *mercury* have many isotopes, but the at. wt. of the different forms have not been determined. The subject of isotopes has been considered by J. J. Thomson, F. A. Lindemann, F. Soddy, F. W. Aston, and T. R. Merton. There is also F. W. Aston's review, *Isotopes* (London, 1922). The isotopes in the radium-uranium family are considered later.

Atoms and molecules with multiple charges.—Any given gas furnishes a number of different curves showing the presence of positive ions with multiple charges. Thus, with oxygen, in addition to (1) ordinary neutral molecules, O_2; and (2) neutral atoms, O; effects were obtained corresponding with streams (3) of atoms with one positive charge, $O^{\cdot}$; (4) of atoms with two positive charges, $O^{\cdot\cdot}$; (5) of atoms with one negative charge, O'; (6) of molecules with one positive charge, $O^{\cdot}_2$; (7) ozone

with one positive charge, O'_3; and (8) molecules O_6 with a positive charge, O'_6. With hydrogen, evidence of entities H, H_2, H', H'', and H'_2 was obtained. T. R. Wilkins estimated that in air, out of 350 positive ions in air, only 3 per cent. were doubly charged; with helium, 10 per cent. were doubly charged; and with hydrogen, 0·5 per cent.

Intermediate stages of chemical action.—The photographic plate registers the rays within a millionth of a second after their formation, so that if a chemical reaction were taking place in the tube, it is possible that the method would disclose the existence of transient intermediate compounds as well as the final products of the reaction. For example, with *methane*, CH_4, five lines occur corresponding with particles having masses 12, 13, 14, 15, and 16. These must correspond with particles having the composition, C, CH, CH_2, CH_3, and CH_4. *Phosgene*, $COCl_2$, furnishes lines corresponding with particles having masses 99, 28, and 35·5, hence the decomposition proceeds by a separation of chlorine atoms from carbon monoxide without rupture of the carbon and oxygen atoms. No signs of a molecule NO_3 were observed during the oxidation of nitric oxide, NO, by oxygen.

Atomic weights.—The parabolic tracks recorded on the photographic plates enable the at. wt. of a gaseous substance to be determined within one per cent. of its true value without requiring more than 0·00001 grm. of the substance. The result, moreover, is not dependent upon the purity of the material, for impurities merely produce additional lines in the positive ray spectrum, and do not affect the curves produced by the substance under examination. The gases evolved from platinum by cathodic bombardment contained H', H_2', C', O', Ne', O_2', and an unrecognized element.

New elements.—If a spectroscopist observed an unknown line in the spectrum of a discharge tube, he would infer the existence of an unknown substance provided the line were not produced by some alteration in the condition of the discharge; similarly, if a new curve be obtained in the positive ray spectrum, the probable existence of a new element would be inferred. Thus, atm. nitrogen gives a curve corresponding with a substance having an at. wt. 40 times that of a hydrogen atom, and is not indicated on the plate when chemically prepared nitrogen is employed. The positive ray method, too, is far more delicate than spectrum analysis, for it enables a foreign gas to be detected in quantities too minute to be revealed by the spectroscope.

Allotropic hydrogen.—J. J. Thomson finds that a gas with at. wt. 3 is given off by most solids when bombarded by the cathode rays. It is interesting to remember that D. I. Mendeléeff (1871) predicted a new element of the halogen group with an at. wt. 3, but J. J. Thomson thinks that the gas in question is a triatomic molecule of hydrogen, H_3, mainly because (1) deliquescent salts or salts containing combined hydrogen—*e.g.* KOH, $CaCl_2$, LiOH—give continuous yields of the gas, while the supply with salts which do not contain combined hydrogen—*e.g.* LiI, Li_2CO_3, KCl—is soon exhausted. (2) Attempts to obtain spectroscope evidence of the new gas gave bright hydrogen lines with traces of mercury—derived from the apparatus used in manipulating the gas. (3) Vigorous sparking in the presence of oxygen, or contact with glowing copper oxide (or even exposure to bright light) destroys the gas. Assuming the gas is really H_3, it is more stable than ozone, more stable indeed than any known allotropic form of an element. If hydrogen is univalent, it is difficult to reconcile its existence with the ordinary views about valency. J. J. Thomson explains it by assuming that the hydrogen atom with its positive nucleus and negative corpuscles exerts a force analogous with that exerted by a magnet; and a group of three atoms can arrange themselves about their axes to form a closed stable ring.

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CHAPTER XXVI

RADIUM AND RADIOACTIVITY

§ 1. Becquerel Rays

The secret of all who make discoveries is to look upon nothing as impossible.—J. von Liebig.

About the time W. C. Röntgen [1] discovered the peculiar X-rays, radiating from phosphorescing Crookes' tubes, H. Becquerel repeated some experiments of A. Niépce de St. Victor in order to find "if the property of emitting very penetrative rays is intimately connected with phosphorescence." In other words, does the principle of reversibility apply? If Röntgen's rays make a fluorescent substance shine in the dark, will a fluorescing substance emit invisible penetrative rays? C. Henry, G. H. Niewenglowsky, and H. Becquerel found that insolated calcium sulphide can, in the dark, send out rays which pass through black paper, and fog a photographic plate; L. Troost, and W. Arnold made a similar observation with respect to zinc blende. H. Becquerel placed fragments of several uraniferous phosphorescent substances on photographic plates wrapped in two sheets of black paper. In about 24 hours, when the plates were developed, a silhouette of the phosphorescent substance appeared on the plate. Hence, it was inferred that "*the phosphorescent salts of uranium must emit radiations which are capable of passing through black paper opaque to ordinary light, and of reducing the silver salts of the photographic plate,* even when the uranium compound has been completely sheltered from the light." These conclusions were confirmed by J. Elster and H. Geitel, P. Spies, A. Miethe, G. C. Schmidt, and M. S. Curie. The radiations emitted by the phosphorescent substance are called **Becquerel rays,** though A. Niépce de St. Victor, thirty years previously, noticed that uranium salts could affect photographic plates in the dark, and G. le Bon called the radiations *lumière noire,* or black light. At first, H. Becquerel thought that these radiations were *lumière emmagasinée*—stored-up light—a kind of invisible phosphorescence; and he inferred that the radiations were identical with light rays in that they could be refracted, reflected, and polarized. The alleged facts were afterwards shown to be wrong, and the inference fallacious.

A substance which possesses the property of emitting these penetrative rays is said to be radioactive, and the property itself is called **radioactivity.** All substances containing uranium are radioactive. The energy is not stored like light in a phosphorescent substance, because the property is no different whether insolated or non-insolated uranium be used; the energy does not come from the air, because it is not affected by confining the uranium in a vacuum. It is therefore probable that the uranium is slowly undergoing some spontaneous change as an effect of its internal energy. Radioactivity does not depend upon light or heat; the emission of the rays appears to be a permanent and abiding property of uranium and its compounds; and it is independent of temp. and of all known physical conditions. No sign of a diminution or increase of the property has been detected whether the substance be heated towards 2000° or cooled towards −200°. A. Piccard and G. Volkart showed that with a magnetic field of 83,000 gauss, no variation of the order 1 per 1000 could be detected. The same weight of uranium, no matter how combined, emits the same amount of radiation. *The chemical*

properties of the elements—excepting perhaps the helium family—can be modified and controlled by changes in the chemical and physical conditions; but radioactivity is independent of these conditions. Consequently, the assumption is made that **radioactivity is an infra-atomic property,** and is not the same type of phenomenon as an ordinary chemical reaction. If chemistry be confined to the study of phenomena with the atom as unit, radioactivity regarded as an infra-atomic phenomenon, is a kind of *meta-chemistry.*

G. C. Schmidt found that thorium is radioactive in the same sense that uranium is radioactive, and these two elements have the highest at. wt.—Th, 232; U, 238. The radioactivity of thorium is readily shown by flattening an ordinary new gas mantle on the sensitive side of a photographic plate, and leaving all in darkness for about a week. When the plate is developed in the usual way, a photograph of the flattened mantle will be produced. The mantle contains sufficient thorium, as oxide, to demonstrate the effect.

H. Becquerel also found that when uranium is brought near to a charged gold-leaf electroscope, the gold-leaf gradually collapses. The rate at which an electroscope is discharged is a measure of the efficiency of the specimen in emitting rays. The charged electroscope, indeed, is more sensitive than the photographic plate for detecting Becquerel rays. Air which has been in contact with uranium and its compounds, like air which has been exposed to Röntgen rays, will discharge an electroscope, for exposure to these radiations makes air a conductor. It will be shown later that Becquerel's rays are complex, for they include the so-called α-rays analogous with the canal rays; β-rays analogous with the cathode rays; and γ-rays analogous with X-rays. S. Meyer and K. Przibram studied the coloration and luminescence of kunzite, glass, quartz, etc., by Becquerel's rays.

As indicated in connection with the union of hydrogen and chlorine, J. J. Thomson [2] failed to detect any sign of ionization during this reaction; G. Kümmell reported evidence to the contrary, but M. le Blanc and M. Vollmer confirmed J. J. Thomson's observation. L. Bloch considers that it is doubtful if any ionization occurs during the reaction between ammonia and hydrogen chloride; and none was observed in the oxidation of nitrogen peroxide, of sulphur dioxide, and of sulphur; or in the union of hydrogen with sulphur. A. Pinkus and M. de Schulthess observed ionization during the reaction of nitric oxide with oxygen or with chlorine; the action of ozone on nitric oxide or nitrogen peroxide; and in the decomposition of ozone. The failure of M. Trautz and F. G. Henglein to detect ionization is attributed to unfavourable conditions of measurement. M. de Broglie and L. Brizard concluded that chemical action produces ionization only when accompanied by a physical reaction such as the passage of a gas through liquid μ, breaking of a crystalline surface, luminescence, etc. They state that there is no ionization in the case of reactions of the following classes: (1) Between gases in the cold; (2) double decomposition in liquids; (3) dry decomposition of amorphous substances at slightly elevated temp.; (4) rupture of an inactive surface by bubbling, while there is ionization in the following cases: (1) Gases prepared by wet way; (2) vigorous reactions by projection into water; (3) dry actions accompanied by the decrepitation of crystals; (4) oxidation of sodium by moist oxygen—feeble ionization; (5) reactions with incandescence, such as flames, or combustion of metals in oxygen or chlorine; (6) reactions with luminescence, such as the oxidation of phosphorus and of quinine sulphate.

In 1782, A. L. Lavoisier and P. S. de Laplace [3] noted that when a cylinder of coal is burning, the cylinder is negatively electrified, and the ambient gas becomes positively electrified. C. S. M. Pouillet made a similar observation with respect to burning carbon, and burning hydrogen. A. L. Lavoisier and P. S. de Laplace also noted that the hydrogen liberated by the action of sulphuric acid on iron is positively electrified. The phenomenon has been investigated by J. Enright, and J. S. Townsend. There are several other strictly chemical reactions—hydration of quinine or cinchonine sulphate; [4] action of sodium amalgam or calcium carbide

on water ;[5] oxidation of phosphorus ;[6] the formation of oxygen by the action of manganese dioxide on hydrogen peroxide ;[7] the formation of ozone ; the action of water vapour, chlorine, the hydrogen halides, and carbonyl chloride on alloys or amalgams of the alkali metals results in the metal acquiring a positive charge and the ambient atm. becomes negatively charged ;[8] in the explosion of a mixture of hydrogen and oxygen ;[9] in the action of carbonyl chloride, chlorine, and water on potassium-sodium alloys ;[10] etc.—which have the power of rendering the ambient air a conductor of electricity so that it can discharge a charged electroscope ; and an attempt has been made to find if the two phenomena are related. The temp. at which hydrogen and oxygen begin to combine in contact with carbon or platinum is almost the same, within the limits of the errors of measurement, as that at which these elements begin to form negatively charged electrons. This, however, is not sufficient to justify a belief that there is a *causal nexus* between the two phenomena. The property exhibited by many chemical reactions of making the ambient air electrically conducting must be sharply distinguished from radioactivity.

E. Rutherford has emphasized the fact that the activity of radioactive bodies has these special characteristics : (1) It is spontaneous ; (2) It is exhibited by all the compounds of the radioactive elements ; (3) It is not altered by changes in the physical or chemical conditions of the element ; (4) The reaction is exothermal, but the speed of the decomposition is not affected by any known external condition ; the thermal value of the reaction, too, is more than a million times greater than that of any known chemical reaction ; (5) The decomposition proceeds in a series of stages—consecutive reactions ; (6) Helium is one ultimate product of the decomposition ; (7) Three types of "radiant rays" are emitted at different stages of the decomposition, which may ionize the ambient air, produce luminescent effects, and induce chemical changes.

A. Schuster[11] expressed the idea that usually when a physical property has been discovered in one element, it will be found to be shared in varying degrees by all the other elements ; and consequently radioactivity may prove to be a common property of all matter. In that case, the so-called radioactive bodies may be distinguished from others—like iron in the case of magnetism—by the enormously exaggerated forms in which they possess the property. The apparently inactive metals may possess radioactivity, but to so small a degree, that our powers of observation are insufficient to detect it. M. S. Curie examined a number of substances to find if any other radioactive elements exist in addition to the uranium-radium family, and to the thorium and actinium families, and found that none have a radioactivity even $\frac{1}{100}$th of that of uranium. J. J. Thomson reported that potassium and rubidium, in vacuo, emit electrons while in darkness. N. R. Campbell and A. Wood tried to find if radioactivity could be detected in other elements, and found that potassium and rubidium both emit β-rays, but no α-rays. The β-ray activity of potassium is not more than $\frac{1}{1000}$th of that of uranium ; and that of rubidium about $\frac{1}{10}$th that of potassium. N. R. Campbell, M. Levin and R. Ruer, E. Henriot, W. W. Strong, H. Lachs, K. Bergwitz, H. Thirring, W. Biltz and E. Marcus, J. W. Woodrow, R. J. Strutt, E. Müller, L. Dunoyer and E. H. Büchner also found that the salts of these two elements emit feeble radiations which affect a photographic plate. The radioactivities of rubidium and potassium are atomic qualities. There is no evident reason why elements of such low at. wt. should exhibit radioactivity. The phenomenon has not been observed with sodium or cæsium. Therefore, while between 30 and 40 radioactive bodies are assumed to exist, not half a dozen of these bodies have been isolated. The properties of those radioactive elements which have not been isolated have been deduced from their behaviour when mixed with large proportions of other known elements. J. C. McLennan and W. T. Kennedy showed that the radioactivity of potassium and rubidium is not due to the action of the γ-rays known to be present in the atm. J. Elster and H. Geitel, and J. Satterly found the quantity of radium in these elements too small to produce the given effect. No success has attended the

efforts of N. R. Campbell, J. Elster and H. Geitel, and E. Henriot to concentrate the active constituent from potassium. E. Rutherford added that the fact that α-rays are absent is taken to mean that the β-radiation cannot arise from the presence of a known β-ray product which is separated with the potassium; for no β-ray product of long period is known which is not transformed into an α-ray product. O. Hahn and M. Rothenbach estimate the half-life period of rubidium to be 10^{11} years, and that of potassium, 3 to 7 times more.

G. le Bon [12] repeatedly affirmed that radioactivity is a universal phenomenon. The atoms of simple bodies, said he, emit emanations of the same family as the cathode rays. H. Geitel, C. T. R. Wilson, R. J. Strutt, N. R. Campbell, J. C. McLennan and E. F. Burton, H. L. Cooke, C. S. Wright, J. Elster and H. Geitel, G. Hoffmann, etc., have studied the phenomenon. Radioactivity is detected by the action of matter on a charged electroscope. The ionization, said E. Rutherford, may be due to one or more of the following effects: (i) the presence of a small quantity of radium emanation mixed with the air; (ii) a superficial activity due to the exposure of the metal to the radioactive matter present in the atm.; (iii) the presence of traces of known types of radioactive matter throughout the volume of the metal; (iv) the escape of a radioactive emanation from the metal into the gas; and (v) the effect of the penetrating γ-rays which arise from the earth and atm. After discussing each of these effects, he concludes:

> Considering the evidence as a whole, there does not seem to be any adequate proof that ordinary metals possess an intrinsic activity corresponding to the well-known radioactive elements. The very weak activity actually observed is in all probability to be ascribed to the presence of traces of radioactive matter as impurities.

G. Hoffmann came to a somewhat similar conclusion in attempting to decide if all the elements are radioactive. J. H. Vincent said that the radioactivity of ordinary elements cannot be detected because of the low velocities of the emitted particles.

It is difficult to communicate a charge of electricity to a gas under normal conditions. This is shown by the insulating properties of air screened from ultra-violet light, and other agents which act on the gas, making it a conductor of electricity. Myriads of gaseous molecules per second may bombard a charged metal plate and rebound without electrification. B. Franklin [13] mentioned that the vapour rising from an electrified water is not itself electrified; and L. J. Blake, H. Pellat, H. Beggeroff, J. C. Beatie, L. Sohncke, and G. Schwalbe also found that the vapour arising from boiling mercury is not electrified, however strongly the liquid be electrified. As J. J. Thomson [14] expressed it, "when an electrified liquid co-operates, the electrified particles are left behind, just as a salt in soln. is left behind on evaporation." Air, however, does become a conductor of electricity when exposed to various other influences, ultra-violet light, hot metals, certain chemical reactions—*vide supra*—etc. This subject is discussed in J. J. Thomson's *Conduction of Electricity through Gases* (Cambridge, 1903). Gases can be electrified by the splashing of liquids, so that the air in the vicinity of a waterfall, where the water falls upon rocks and breaks into spray, is electrified. P. Lenard showed that a positive charge goes to the water, and the air is negatively electrified. Lord Kelvin noted that air which has bubbled through water is negatively electrified. J. J. Nolan has discussed the ionization of air by splashing water. J. J. Thomson found that the effect produced by dil. soln. of some salts, etc., is very great; but H. Zwaardemaker and H. Zeehuisen found that purified water and most inorganic salt soln. give no charge to water spray.

C. du Fay,[15] E. F. du Tour, and others knew in the eighteenth century that the air in the vicinity of hot metals becomes a conductor of electricity, and many observations have been made on the subject since that time. The subject has been discussed in O. W. Richardson's monograph *The Emission of Electricity from Hot Bodies* (London, 1916). It is shown that the number of electrons emitted per

unit area of surface increases rapidly with temp., $T°$ K., according to the formula $i=aT^{\frac{1}{2}}e^{-b/T}$, where a and b are constants, and i denotes the current per unit area. The ratio e/m for the electrons emitted by hot bodies is the same as that obtained for the cathode rays. Early in the nineteenth century, A. Volta [16] found that flames are conductors of electricity, but the results of many subsequent observers are obscured by the conductivity induced by incandescent wires. The conductivity of gases containing salt vapours, and the flow of electricity through salt-laden flames, has been investigated by S. Arrhenius,[17] etc. H. A. Wilson found that, under similar conditions with respect to temp., potential difference, and conc., the conductivity imparted to the flame by cæsium, rubidium, potassium, sodium, lithium, and hydrogen chlorides or nitrates decreased in the order named. The subject is discussed in H. A. Wilson's *The Electrical Properties of Flames and of Incandescent Solids* (London, 1912). H. Hertz's discovery [18] that the incidence of ultra-violet light on the spark gap facilitated the passage of the spark, was immediately followed by numerous investigations of the action of light, and of ultra-violet rays on the discharge of electricity from charged bodies—*vide* photochemical effect. The subject is discussed in the monographs, A. L. Hughes, *Photoelectricity* (Cambridge, 1914), and H. S. Allen, *Photoelectricity* (London, 1913). W. C. Röntgen [19] noted the ionization produced in gaseous media by X-rays. J. S. Townsend [20] has shown that gases may be ionized by the collision of the molecules with fast-moving positive or negative ions. The subject is discussed in his monograph, *The Theory of Ionization of Gases by Collision* (London, 1910); and also by B. Bianu, P. O. Pedersen, and J. Franck and co-workers. The ionization of gases by Becquerel's rays from radioactive uranium, etc., has been studied by H. Becquerel,[21] etc. The subject of radioactivity is discussed in the monographs, M. S. Curie, *Traité de radioactivité* (Paris, 1910); E. Rutherford, *Radioactive Substances and their Radiations* (Cambridge, 1913); S. Meyer and E. von Schweidler, *Radioaktivität* (Leipzig, 1916); F. Henrich, *Chemie und chemische Technologie radioaktiver Stoffe* (Berlin, 1918); W. H. Bragg, *Studies in Radioactivity* (London, 1912); F. Soddy, *The Chemistry of the Radioelements* (London, 1911–4).

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§ 2. Radium

It is the glory of God to conceal a thing, but the glory of a king to search it out.—Solomon.

For even the things which be in our hands—
These, knowing, we know not—so far from us,
In doubtful dimness, gleams the star of truth.
Anon.

Is the radioactivity of uranium due to the presence of an impurity?—In 1898, P. and M. S. Curie,[1] and G. Bémont found that the radioactivity is due to the presence of *une nouvelle substance fortement radioactive, contenue dans la pechblende;* and in her thesis: *Recherches sur les substances radioactives* (Paris, 1903), Marya Sklodowska Curie examined the radioactivity of a number of uranium minerals and other substances. She found the following relative radioactivities, expressed in units $\times 10^{-11}$ ampères:

	Units.		Units.
Pitchblende (Johanngeorgenstadt)	8·3	Ammonium uranite	1·3
Pitchblende (Joachimstahl)	7·0	Sodium uranate	1·2
Pitchblende (Przibram)	6·5	Uranyl sulphide	1·2
Carnotite	6·2	Samarskite	1·1
Chalcolite	5·2	Uranyl sulphate	0·7
Autunite	2·7	Potassium uranyl sulphate	0·7
Metallic uranium	2·3	Aeschynite	0·7
Orangite	2·0	Uranium nitrate	0·7
Uranium oxide (green)	1·8	Monazite	0·5
Pitchblende (Cornish)	1·6	Fergusonite	0·4
Uranic acid	1·6	Niobite	0·3
Thorium oxide	0·14	Xenotime	0·03
Cleveite	1·4	Tantalite	0·02

Obviously some uraniferous minerals are more active than uranium itself. Hence, it was inferred that " the strong activity of the pitchblende from Joachimstahl (Bohemia) is due to the presence of small quantities of a substance wonderfully radioactive, and different from uranium or any other simple body known." This result was confirmed by the extraction of the chloride of what was supposed to be a new element designated **radium,** Ra. The salt was over a million times more radioactive than uranium.

In its general chemical behaviour, radium resembles barium, and the first stage of the extraction of radium from its ores resembles the process which would be employed if barium was to be extracted. In the extraction, polonium accumulates with the bismuth and actinium with the rare earths. The separation of radium from pitchblende is conducted in three stages: (i) The separation of uranium from the ore; (ii) the extraction of a mixture of radium and barium bromides or chlorides from the residue; and (iii) the separation of the two chlorides by fractional crystallization—the radium salt has the lower solubility, and if a sat. soln. of the mixed chlorides is raised to boiling, and allowed to cool, the small part which crystallizes out is five times more radioactive than the part remaining in soln.

The chief mineral employed for the extraction of radium is pitchblende, which is found in commercial quantities in Bohemia, South Saxony, Cornwall, Gilpin County (Cal.), etc. The minerals uranite, samarskite, and brannerite rarely occur in commercial quantities. By weathering, they furnish autunite, torbernite, carnotite, and tyuyamunite. The two latter are the most abundant and furnish the bulk of the world's supply. They are found in S.-W. Colorado and S.-E. Utah; smaller quantities of carnotite occur near Olary (S. Australia). Tyuyamunite occurs in Tyua-Muyun (Russian Turkestan). R. M. Kehny, C. H. Viol, and H. Foley have discussed the production and uses of radium. One ton of pitchblende, containing about 0·37 grm. of radium, furnished about half of this amount by the following method of extraction.

The powdered mineral is first roasted with sodium carbonate, and the product washed with warm water to remove the excess of sodium carbonate, and then with dil. sulphuric acid. The uranium passes into soln., and the insoluble residue contains sulphates of radium, calcium, lead, barium, etc., silica, and a small proportion of copper, zinc, aluminium, thallium, the rare earths, arsenic, antimony, bismuth, vanadium, tantalum, columbium, manganese, iron, cobalt, nickel, etc. The residue is $1\frac{1}{2}$ to $4\frac{1}{2}$ times as radioactive as metallic uranium. 10,000 kgrms. of pitchblende ore yield 3000 kilogrms. of residue.

In M. S. Curie's system, which includes A. Debierne's suggestions, the residue is treated by the following process: Radium sulphate is the least soluble sulphate in the residue, and to dissolve it, the sulphuric acid should be as far as possible removed. The residue is accordingly boiled with a conc. soln. of sodium hydroxide, and washed. Sodium sulphate, and lead, silica, and alumina are removed with the alkaline soln., and the washing. The insoluble residue is digested with hydrochloric acid; the material is disintegrated and most of it is dissolved. *Polonium* may be obtained by precipitation with hydrogen sulphide, and the filtrate, oxidized with chlorine, and treated with ammonia, gives a precipitate containing *actinium*. The barium and radium remain as undecomposed sulphates in the portion not dissolved by hydrochloric acid. The insoluble matter is washed and then boiled with a soln. of sodium carbonate; the barium and radium sulphates are transformed into carbonates. The washed residue is treated with dil. hydrochloric acid free from

sulphuric acid. The filtered soln. contains barium, radium, and some polonium, and actinium; it is treated with sulphuric acid when a mixture of sulphates of barium, radium, calcium, lead, and iron, with a trace of actinium, is precipitated; the filtrate contains a little actinium and polonium, which can be recovered as before. A ton of residue gives between 10 and 20 kgrms. of crude sulphate with a radioactivity about 60 times that of metallic uranium.

The crude sulphates are purified by boiling with a soln. of sodium carbonate, and the resulting carbonates dissolved in dil. hydrochloric acid. As before the soln. is treated with hydrogen sulphide for polonium; oxidized with chlorine, and treated with ammonia for actinium. The filtrate is precipitated with sodium carbonate; and the washed carbonates again converted into chlorides by treatment with dil. hydrochloric acid. The soln. is evaporated to dryness, and washed with conc. hydrochloric acid. Nearly all the calcium chloride dissolves while the barium and radium chlorides remain ready for fractionation. A ton of residue gives about 8 kgrms. of the mixed chlorides, whose radioactivity is about 60 times that of metallic uranium. The mixed chlorides are dissolved in water, the soln. boiled, and allowed to cool. The crystals, *C*, which separate are more active than those obtained by evaporating the mother liquid, *S*. The operation is then repeated with each portion *C* and *S*. This gives four portions. The less active fraction of *C* is added to the more active portion of *S*. The operation is now repeated with the resulting three portions. The scheme is shown diagrammatically in Fig. 1. After each series of operations, the sat. soln. arising from one fraction is added to the crystals arising from the following fraction; but if after one of the series the most soluble fraction has been withdrawn, then, after the following series, a new fraction is made from the most soluble portion, and the crystals of the most active portion are withdrawn. By the successive alternation of these two processes, an extremely regular system of fractionation is obtained, in which the number of fractions and the activity of each remains constant, each being about five times as active as the subsequent one, and in which, on the one hand, an almost inactive product is removed, whilst, on the other, is obtained a chloride rich in radium. The amount of material contained in these fractions gradually diminishes, becoming less as the activity increases. The number of portions is not allowed to increase indefinitely. The activity of the most soluble portion diminishes as the number increases. When its activity becomes inconsiderable, it is withdrawn from the fractionation. When the desired number of fractions has been obtained, fractionation of the least soluble portion (the richest in radium) is stopped, and it is withdrawn from the remainder. At first, six fractions were used, and the activity of the chloride obtained at the end was only one-tenth of that of uranium. When most of the inactive matter has been removed, and the fractions have become small, one fraction is removed from the one end, and another is added to the other end, consisting of the active chloride previously removed. A chloride richer in radium than the preceding is thus obtained. This system is continued until the crystals obtained are pure radium chloride. If the fractionation has been thoroughly carried out, scarcely any trace of the intermediate products remains. At an advanced stage of the re-fractionation, when the quantity of material in each fraction is small, the separation by crystallization is less efficacious, the cooling being too rapid and the volume of the soln. to be decanted too small. It is then advisable to add water containing a known quantity of hydrochloric acid; this quantity may be increased as the fractionation proceeds. The advantage gained thus consists in increasing the quantity of the soln., the solubility of the chlorides being less in water acidified with hydrochloric acid than in pure water. By using water containing much acid, excellent separations are effected, and it is only necessary to work with three or four fractions.

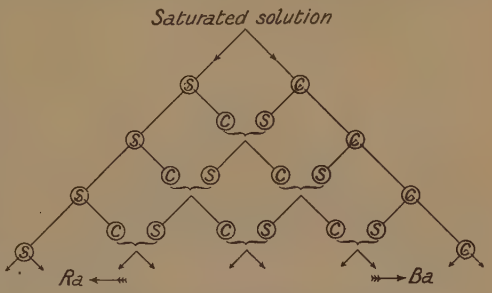

FIG. 1.—Scheme of Fractional Crystallization of Radium and Barium Chlorides.

The crystals, which form in very acid soln., are elongated needles, those of barium chloride having exactly the same appearance as those of radium chloride. Both show double refraction. Crystals of barium chloride containing radium are colourless, but when the proportion of radium becomes greater, they have a yellow coloration after some hours, verging on orange, and sometimes a beautiful pink. This colour disappears in soln. Crystals of pure radium chloride are not coloured, so that the coloration appears to be due to the mixture of radium and barium. The maximum coloration is obtained for a certain degree of radium present, and this fact serves to check the progress of the fractionation. The fractional precipitation of an aq. soln. of barium chloride by alcohol also leads to the isolation of radium chloride, which is the first to precipitate. This method, which was first employed, was finally abandoned for the one just described, which proceeds with more regularity.

M. S. Curie, however, occasionally made use of precipitation by alcohol to purify radium chloride which contains traces of barium chloride. The latter remains in the slightly aq. alcoholic soln., and can thus be removed. F. Giesel and H. Paweck recommended the separation of barium and radium by fractional crystallization in water from a mixture of the bromides. This method is advantageous, especially in the first stages of the fractionation. C. E. Scholl also obtained good results with the bromides. For the isotopic meso-thorium *vide* thorium.

Many modified proposals have been made of the method of extraction employed by M. S. Curie. These different methods of treating radium ores can be classed: (i) Leaching the ore with sulphuric acid (H. Fleck, W. G. Haldane, and E. L. White; and H. N. McCoy); hydrochloric acid, or nitric acid (C. L. Parsons and co-workers, R. B. Moore and K. L. Kithil, and G. A. Koenig); (ii) Leaching the ore first with an alkali, and then with an acid—*e.g.* J. H. Haynes and W. D. Engle, H. M. Plum, and W. F. Bleecker digested the ore with a soln. of sodium carbonate, and digested the residue with dil. hydrochloric or nitric acid; L. Haitinger and C. Ulrich extracted pitchblende with alkali-lye and then dissolved it in dil. sulphuric acid; and (iii) Fusing the ore with some material which will open the ore—*e.g.*, W. F. Bleecker roasted the ore with sodium chloride and hydroxide; S. Radcliff fused the ore with sodium hydrosulphate; F. Ulzer and R. Sommer also used an alkali hydrosulphate; and E. Ebler roasted the material with lime or calcium carbonate and sodium and calcium chloride. E. Ebler and A. J. van Rhyn extracted more than 80 per cent. of the radium as crude sulphate, from earths poor in radium, by the following process:

The powdered mineral is mixed with about an equal weight of sodium or calcium chloride and calcium carbonate, and heated at the sintering temp. (800°–1000°) for five or six hours in a muffle furnace. The cooled mass is powdered and extracted with dil. hydrochloric acid containing sulphuric acid and barium chloride. The sulphate precipitate containing the radioactive material can then be readily washed away from the coarse inactive particles and filtered off. The weight of crude sulphates obtained is about 7 per cent. of the original ore. This method was used to extract radium from Portuguese torbernite ore containing only $4{\cdot}5\times10^{-7}$ per cent., from Colorado carnotite sandstone containing $5{\cdot}0\times10^{-7}$ per cent., and from Mexican pitchblende-quartzite containing $2{\cdot}84\times10^{-7}$ per cent. of radium.

In R. B. Moore and K. L. Kithil's nitric acid process for extracting radium from carnotite, the powdered ore is heated with nitric acid and the insoluble residue discarded. H. D. d'Aguiar has described this process. The nitric acid soln. is treated with sulphuric acid when radium and barium sulphates are precipitated, while the vanadium and uranium salts remain in soln. The sulphates are reduced to sulphides, converted into chlorides, and fractionally crystallized.

W. Marckwald found that on adding a conc. aq. soln. of a mixture of radium and barium chlorides to a one per cent. sodium amalgam, part of the sodium in the amalgam is displaced by an eq. quantity of radium and barium, the proportion of radium absorbed being greater than that of barium; on decomposing the amalgam with hydrochloric acid, the metallic chloride obtained is much more active than the original salt. By repeating this process, a much enriched salt is obtained, but the manipulation is tedious, and the method offers little advantage over the ordinary one of fractional crystallization. Instead of converting the sulphates to chlorides by the tedious process of A. Debierne and M. S. Curie, it is advantageous, in many cases, to reduce the sulphates to sulphides and dissolve the latter in hydrochloric acid; thus E. Ebler reduced with calcium carbide: $MSO_4+4CaC_2=4CaO+MS+8C$; and E. Ebler and M. Fellner, with calcium hydride: $MSO_4+4CaH_2=4CaO+MS+4H_2$; C. L. Parsons and co-workers tried reducing with carbon: $MSO_4+4C=MS+4CO$; F. Soddy, and C. L. Parsons also suggested coal gas; and F. Soddy, water gas. E. Ebler and W. Bender compared the different processes and obtained better results with the strongest reducing agent. O. Hönigschmid heated the sulphate in a mixed vapour of carbon tetrachloride and hydrogen chloride. According to C. L. Parsons and co-workers, the production of a precipitate, or the presence of one, in a radium-barium soln. does not necessarily involve the adsorption of

considerable quantities of radium from soln. As has already been pointed out, the precipitation of 700 grms. of lead sulphide in ammoniacal soln. carried with it only 3 out of 1,500 mgrms. of radium. The work of F. Paneth shows that any serious removal of radium by adsorption is likely to occur only when the radium forms an insoluble salt with the negative radical of the adsorbent. The failure of radium to be removed as sulphide, together with lead sulphide, accords well with its chemical nature, since radium sulphide is soluble. On the other hand, the completeness of its removal as carbonate, which is to be expected, has been shown by the fact that only 6·4 out of 1500 mgrms. of radium passed into 300 litres of filtrate. Even if barium sulphate is present or is precipitated in a soln. containing radium, the amount of radium removed is small provided a large excess of barium is present. F. E. E. Germann found that radium is adsorbed from soln. of its salts by barium sulphate, and the adsorption follows the laws of K. Kröker, and H. Freundlich.

According to A. Coehn, radium is not deposited on a platinum electrode by the electrolysis of soln. in alcohol, acetone, or pyridine, since the cathode shows only a temporary induced activity. With aq. soln., cathodes of different metals acquire only a temporary radioactivity in presence of radium bromide soln.; a mercury cathode, however, becomes permanently active, and when extracted with hydrogen bromide gives a permanently active bromide. The difference of potential required for the separation of a metal (calculated from heats of formation) increases in the series calcium, strontium, and barium, but proceeds in the reverse direction when amalgams are produced, so that the separation of strontium on mercury requires 0·2 volt more than barium, and calcium 0·25 volt more than strontium; this difference is sufficient for the electrolytic separation of these metals. These values, however, are for soln., although the difference between radium and barium should be greater than between barium and strontium. It is not possible to separate these metals except with extraordinarily small current densities; metallic radium is, however, precipitated by barium amalgam. Neither barium nor radium can be separated from aq. soln. by deposition on melted Wood's alloy. Metallic radium cannot be satisfactorily deposited on amalgamated platinum; but can be deposited on amalgamated zinc, the upper part of the rod being protected from oxidation by means of paraffin wax. By precipitation on a pure mercury cathode and dissolution in hydrogen bromide, a considerable increase of activity is obtained in the bromide. A silver anode was used to absorb the bromine; and at first it showed a greater radioactivity than the cathode, but this was due only to an induced radioactivity, and disappeared at the end of 24 hours. The redissolving of the metallic radium in the soln. from which it is being deposited can be greatly checked by using methyl alcohol as the solvent in place of water. Metallic radium in the form of amalgam behaves like its compounds in that the radioactivity increases during several days to a maximum value.

M. S. Curie and A. Debierne prepared radium amalgam by the electrolysis of a soln. of 0·106 grm. of perfectly pure radium chloride with a cathode of mercury (10 grms.) and an anode of platinum-iridium. After electrolysis, the soln. contained 0·0085 grm. of the salt. The amalgam was quite fluid, whereas with barium under similar conditions, the amalgam is partly crystalline. The dried amalgam was transferred to an iron boat and heated cautiously in a quartz tube in a current of hydrogen purified by passage through the walls of a platinum tube heated in an electric furnace. The temp. of the boat was determined by a thermocouple. Most of the mercury was distilled at 270°. At 400° the amalgam became solid, and its m.p. rose progressively as the mercury was driven off to 700°. At this temp. no more mercury volatilized, but the radium itself commenced to volatilize and to attack the quartz tube energetically. The boat now contained a brilliant white metal. It adhered strongly to the iron, and blackened immediately on exposure to air, probably forming the nitride. The penetrating rays from the boat containing the metal, sealed in a glass tube, showed the normal increase follow-

ing the law of production of the emanation. E. Ebler and H. Herschfinkel obtained the more or less impure metal by heating the azide to 180°–250°, when $Ra(N_3)_2 = Ra + 3N_2$.

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§ 3. The Occurrence of Radioactive Substances

In 1902, J. J. Thomson [1] found evidence of electronic activity in the air bubbled through the tap-water of Cambridge; and J. Elster and H. Geitel obtained similar results by drawing air through soils and clays; and the air of caverns was found to be more radioactive than normal atm. air. R. J. Strutt estimated the conc. of radium in a number of soils and rocks from widely different localities. The computation was based on an assumption as to the constant proportion of radium and uranium, which was afterwards shown to be erroneous. The results, corrected by A. S. Eve and D. McIntosh, showed that in 28 igneous rocks, the amount of radium ranges from $0{\cdot}30 \times 10^{-12}$ to $4{\cdot}78 \times 10^{-12}$ grms. per gram of material—the average is $1{\cdot}7 \times 10^{-12}$. The highest values were obtained with granites, and the lowest with basalts and olivine rocks. For sedimentary rocks, the average of 17 determinations was $1{\cdot}1 \times 10^{-12}$ grms. per gram of material. J. Joly found the mean radium content of igneous rocks to be $5{\cdot}5 \times 10^{-12}$, and of sedimentary rocks $4{\cdot}3 \times 10^{-12}$ grms. per gram.

Radium produces a radioactive gaseous emanation which itself gradually changes; if sufficient time be allowed and the mixture is in equilibrium, the amount of emanation is strictly proportional to the amount of the parent radium, so that given the amount of one, the amount of the other can be calculated. Other radioactive elements no doubt play their part, but radium so far preponderates that geochemical radioactivity is commonly stated in terms of radium. Comparative determinations can be made by spreading the dried powdered material over the same area on a plate introduced into the electroscope.[2] The subject has been discussed by S. C. Lind, P. Loisel, P. Ludewig, N. E. Dorsey, H. Greinacher, and O. Nürnberger. In **estimating the amount of radium in rocks and minerals,**

etc., the material is decomposed so as to bring it into soln. and enable the radioactive gas to be isolated. Its amount is then determined by its action on the air within an electroscope. The mineral is fused with sodium carbonate, or potassium hydroxide, and afterwards extracted with water, and the residue, if any, with dil. acid. If the mineral is directly soluble in a given menstruum, there is no need for the fusion process. The mixed soln. is stored for a few weeks in a closed flask, resembling *A*, Fig. 2, so as to allow the equilibrium amount of emanation to develop. To estimate the amount of radium, the flask *A* is attached to a water reflux condenser *B*; and the latter is connected with the rest of the apparatus, Fig. 2, by means of the ground-joint, *G*, held together by steel springs. The emanation is expelled from the flask by vigorously boiling for about an hour. The cooling water is run from the condenser *B*, to allow the steam to drive the emanation into the reservoir *C*. The stopcock is then closed. Meanwhile the air is exhausted from the electroscope by connecting the apparatus with the pump. The air in the

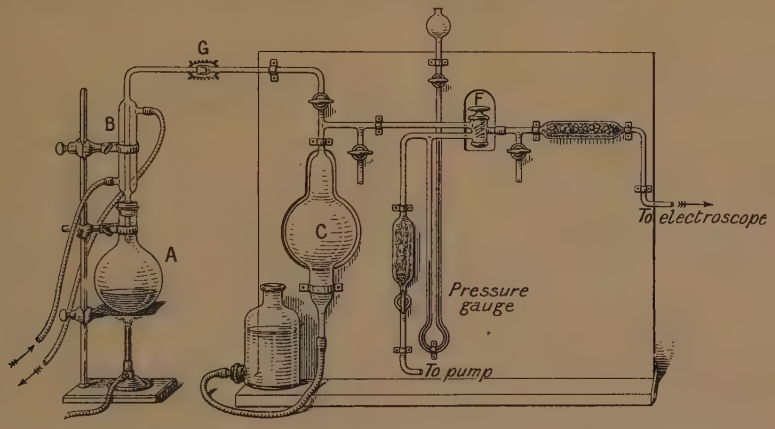

FIG. 2.—The Estimation of Radium in Minerals.

gasholder *C*, charged with the emanation, is cautiously allowed to pass into the electroscope by opening the tap *F*. The rate at which the electroscope is discharged is measured by the number of scale-divisions the leaf of the electroscope falls per hour, and this is assumed to be proportional to the amount of radium in the original mineral. A mineral with a known amount of radium is employed as a standard of reference. The radium can also be computed from the amount of uranium—determined by analysis—in a sample of pitchblende ore, where the ratio uranium to radium is nearly constant, *viz.* one gram of uranium per $3{\cdot}4 \times 10^{-7}$ grms. of radium. Hence, therefore, the amount of uranium as well as of radium in a uraniferous mineral can be estimated by this method. In carnotite, and several other uranium minerals, the ratio of uranium to radium is not always constant and has to be determined by experiment.

EXAMPLE.—R. B. Moore and K. L. Kithil treated 22 mgrms. of a sample of pitchblende, known to contain the eq. of 50 per cent. of uranium; and, 3 hrs. after introducing the emanation to the electroscope, they found the leaf to fall 40·5 divisions per minute. The natural leakage of the instrument was 0·5 division per minute, so that the emanation from the radium in equilibrium with 0·01 grm. of uranium caused the leaf of the electroscope to fall 40 divisions per minute. Hence, a fall of one division per minute represents $0{\cdot}01 \div 40 = 2{\cdot}5 \times 10^{-4}$ grms. of uranium. This is the *constant of the electroscope*. One gram of a given pitchblende ore was fused with sodium carbonate, and at the end of a month, the soln. was treated as above described. In 3 hrs. the leaf of the electroscope fell at the rate of 18·5 divisions per minute. Allowing for the natural rate of the electroscope, the emanation produced a leakage of 18 divisions per minute. Hence, the ore contained $18 \times 2{\cdot}5 \times 10^{-4} = 45 \times 10^{-4}$ grms. of uranium. The ratio of radium to uranium in pitchblende ores is approximately $3{\cdot}4 \times 10^{-7}$ grms. of radium per gram of uranium, one gram of the pitchblende in

question not only contains 45×10^{-4} grms. of uranium, but also $(45\times10^{-4})\times(3{\cdot}4\times10^{-7})=1{\cdot}53\times10^{-9}$ grms. of radium.

Numerous observations have been made on the radioactivity of rocks and minerals.[3] Expressing the results in billionths of a gram per gram of material. A. Holmes found :

		Grm. per gram.
Igneous rocks	Acidic rocks	$3{\cdot}1\times10^{-12}$
	Intermediate rocks	$2{\cdot}1\times10^{-12}$
	Basic rocks	$1{\cdot}1\times10^{-12}$
	Ultrabasic rocks	$0{\cdot}5\times10^{-12}$
Sedimentary rocks	Clays	$1{\cdot}5\times10^{-12}$
	Sandstones	$1{\cdot}4\times10^{-12}$
	Limestones	$0{\cdot}9\times10^{-12}$

The igneous rocks are therefore more radioactive than the sedimentary rocks. J. Joly considers it probable that the uranium is in considerable part removed during the general disintegration of the parent rock ; but the radioactivity of the detrital rocks shows that a proportion of the uranium is retained in the *débris* of the parent rock. Seventeen samples of deep-sea deposits from the *Challenger* expedition were radioactive. According to J. Joly :

Extent in sq. miles	Globigerina ooze. $49{\cdot}5\times10^{6}$		Radiolarian ooze. $2{\cdot}5\times10^{6}$		Red clay. $51{\cdot}5\times10^{6}$	
Calcium carbonate	92·24	64·34	10·19	3·89	28·28	12·00 per cent.
Radium	$6{\cdot}7\times10^{-12}$	$7{\cdot}4\times10^{-12}$	$22{\cdot}8\times10^{-12}$	$50{\cdot}3\times10^{-12}$	$52{\cdot}6\times10^{-12}$	$15{\cdot}4\times10^{-12}$

This shows that the radioactivity and the proportion of calcareous matters stand in an inverse order. The first red clay is exceptional in that the proportion of calcium carbonate is higher than usual ; J. Joly says that it is probable that the lower part of the deposit, richer in calcareous matter, dilutes the more recently formed clay above. J. Joly gives 6×10^{-12} grms. of radium per gram in the material spread on the ocean floor, and hence estimates that there are $11{\cdot}7\times10^{6}$ tonnes of radium spread on the ocean floor.

No marked parallelism has been observed between the acidity of the rocks and their radioactivity. The radium is considered to be an accessory mineral, and different samples of the same kind of rock, even from the same locality, were found by H. Mache and M. Bamberger to give very different results ; and E. H. Büchner found that the radioactivity of the rocks can be better classified geographically than petrographically. From borings taken at different depths, A. S. Eve and D. McIntosh, E. H. Büchner, and H. E. Watson and G. Pal could find no simple relation between the radium content and depth ; nor is there any relation between the geological age and the radioactivity of igneous and sedimentary rocks. J. Joly estimated the radium content of the earth's crust to be $2{\cdot}0$–$2{\cdot}6\times10^{-12}$ grms. per gram. The uranium content is calculated on the assumption that 10^{-12} grms. of radium represent 3×10^{-6} of uranium. The radioactivity of the soil approximates 8×10^{-12} grms. of radium per c.c. J. Joly found the Vesuvian lavas contained $12{\cdot}3\times10^{-12}$ grms. of radium per gram. O. Scarpa also studied these lavas.

R. J. Strutt, G. A. Blanc, J. Joly, and H. Mache and M. Bamberger have discussed the radioactivity due to thorium ; and they conclude that the aggregate radioactivity from this source is not inconsiderable in comparison with that derived from the radium elements. From the estimate of J. Joly, J. H. J. Poole, and A. Holmes, the radioactive thorium in different rocks is as follows :

		Grm. per gram.
Igneous	Acidic rocks	$2{\cdot}33\times10^{-5}$
	Intermediate rocks	$2{\cdot}16\times10^{-5}$
	Basic rocks	$0{\cdot}79\times10^{-5}$
Sedimentary	Clays	$1{\cdot}25\times10^{-5}$
	Sandstones	$0{\cdot}55\times10^{-5}$
	Limestones and dolomites	$<0{\cdot}08\times10^{-5}$

The thorium content is rather greater, but of the same order of magnitude as the uranium content.

It is assumed that there is a genetic relation between uranium and radium—*vide infra*—and this is confirmed by the nearly constant ratio Ra : U, in very old compact and unweathered rocks where it may be assumed that the changes involved are in the steady state. According to J. H. L. Johnstone and B. B. Boltwood, the total activity of uranium in equilibrium with its products is 4·73 times the activity of uranium alone. R. J. Strutt,[4] B. B. Boltwood, and H. N. McCoy found Ra : U$=3{\cdot}4\times10^{-7}$: 1; A. Becker and P. Jannasch obtained $3{\cdot}38\times10^{-7}$ to $3{\cdot}415\times10^{-7}$: 1; and F. Soddy and R. Pirret, $3{\cdot}15\times10^{-7}$: 1; E. Gleditsch, $3{\cdot}22\times10^{-7}$: 1; and S. C. Lind and L. D. Roberts give $3{\cdot}40(\pm0{\cdot}03)\times10^{-7}$—*vide* Table I. W. Marck-

TABLE I.—THE RADIUM-URANIUM RATIO OF SOME RADIOACTIVE MINERALS.

Minerals.	Locality.	Activity.	Radium per cent.	Uranium per cent.	Ratio $\frac{Ra}{U}$
Chalcolite	Saxony	—	$0{\cdot}714\times10^{-5}$	39·29	$1{\cdot}82\times10^{-7}$
Carnotite	Colorado	0·76	0·375 „	16·00	2·34 „
Gummite	Germany	—	0·31 „	12·20	2·54 „
Autunite	Autun	1·52	1·20 „	46·92	2·56 „
Autunite	Tonquin	1·50	1·22 „	47·10	2·59 „
Chalcolite	Germany	1·20	0·905 „	28·80	3·14 „
Pitchblende	Joachimsthal	1·90	1·48 „	46·10	3·21 „
Gummite	Germany	1·23	0·58 „	17·37	3·34 „
Chalcolite	Portugal	1·70	1·30 „	39·03	3·33 „
Samarskite	India	0·42	0·295 „	8·80	3·35 „
Brŏggerite	Norway	3·90	2·10 „	63·89	3·29 „
Clévéite	„	2·96	1·81 „	54·90	3·32 „
Uranothorite	„	0·76	0·16 „	4·83	3·31 „
Fergusonite	„	0·30	0·223 „	6·30	3·55 „
Thorianite	Ceylon	2·32	0·66 „	18·60	3·55 „
Chalcolite	Cornwall	2·00	1·70 „	48·66	3·49 „
Pitchblende	„	1·40	1·07 „	28·70	3·74 „

wald and co-workers found with different samples of pitchblende containing 9·01 to 71·20 per cent. of uranium, and a ratio between $3{\cdot}32\times10^{-7}$ and $3{\cdot}34\times10^{-7}$: 1—mean $3{\cdot}329\times10^{-7}$: 1; thus :

U per cent.	9·01	23·74	41·46	44·53	59·95	63·52	66·55	71·20
$Ra/U\times10^{7}$	3·320	3·339	3·331	3·323	3·328	3·341	3·328	3·235

S. C. Lind and C. F. Whittemore found for carnotites from Colorado and Utah :

U per cent.	1·29	1·78	2·04	3·33	6·60	7·94	20·6	28·18
$Ra/U\times10^{7}$	3·42	3·38	3·58	3·33	4·59	2·99	2·41	3·59

Differences may be anticipated with younger minerals which have not had time to accumulate the maximum value of radium; or with products which have been weathered and leached by water. Thus, J. Danne found a sample of pyromorphite which contained radium and no uranium; H. N. McCoy, however, showed that the radium is confined to a surface layer which had been deposited by flowing water. E. Gleditsch found the ratio with chalcolite to be $1{\cdot}82\times10^{-7}$; with carnotite, $2{\cdot}34\times10^{-7}$; and with autunite, $2{\cdot}58\times10^{-7}$. A. S. Russell, and F. Soddy and R. Pirret, also obtained low results with autunite. The best representative value for the Ra : U ratio in uranium minerals is $3{\cdot}3\times10^{-7}$: 1. Since the uranium content of U_3O_8 is 84·82 per cent., it may there be anticipated that an ore with 50 per cent. of U_3O_8, will contain $1{\cdot}4\times10^{-7}$ grms. of radium per gram of ore; *i.e.* a gram of radium to nearly 7000 kgrms. of ore. There will be about 10–20 per cent. loss of radium in the extraction. The subject has also been investigated by L. Haitinger and C. Ulrich, H. Souczek, S. Meyer and V. F. Hess, A. Muguet and J. Seroin, etc.

From the fact that radioactive substances constantly emit heat, and since the emanations are ubiquitous in the earth's crust, it follows that the heating effects of these substances must play an important part in maintaining the heat of the earth, and must have profoundly modified the rate of cooling of the earth in past ages.[5] Attempts have also been made by B. B. Boltwood,[6] and A. Holmes to calculate the age of rocks and minerals from the ratio Pb/U, making certain assumptions as to the relations of the two elements; R. J. Strutt,[7] and J. A. Gray dealt likewise with the helium and uranium or radium ratio; but A. Piutti showed that the ratio is too irregular to justify any calculations. The smaller circular spots, called *pleochroic haloes*, found in brown mica, *e.g.* biotite—in cordierite, and in some other minerals are assumed to be caused by the radioactive properties of a centrally placed mineral particle. They have been studied by O. Mügge, J. Joly and E. Rutherford;[8] and they have been used in attempts to estimate the ages of the minerals in which they occur. J. Joly inferred from the peculiarities of some haloes in the Ytterby and Arendal micas that a new radioactive exists emitting an α-ray with a range of about one cm. in air; and he called this hypothetical element *hibernium* (Hibernia or Ireland).

The waters of the ocean and inland seas are radioactive. Estimates have been made by R. J. Strutt,[9] A. S. Eve, J. Satterly, etc. J. Joly found for the waters of the Atlantic ocean from $0{\cdot}007\times10^{-12}$ to $0{\cdot}038\times10^{-12}$ grms. per c.c.; the Indian Ocean, $0{\cdot}004\times10^{-12}$ to $0{\cdot}009\times10^{-12}$ grms. per c.c.; the Arabian Sea, $0{\cdot}027\times10^{-12}$ grms. per c.c.; the Mediterranean Sea, $0{\cdot}008\times10^{-12}$ grms. per c.c.; and for the Black Sea, $0{\cdot}007\times10^{-12}$ grms. per c.c. The average of all 24 determinations is $0{\cdot}017\times10^{-12}$ grms. per c.c. J. Joly estimates that there are 20×10^{9} grms., or about 20,000 tonnes of radium in the waters of the ocean—assumed to be $1{\cdot}452\times10^{-18}$ tonnes. The water from deep-seated springs and wells[10] has usually a marked radioactivity, which is attributed by F. Himstedt to deep-seated radioactive minerals. It has been stated that the curative properties of certain mineral waters—*e.g.* those of Buxton, Bath, Wiesbaden, Bohemia, etc.—are due to their radioactivity. This statement is mere guessing, because so little is known about the physiological action of the radiations from radioactive materials.

In 1900, H. Geitel showed that one or more radioactive substances are everywhere present in the atm.,[11] and C. T. R. Wilson showed that an insulated electrified conductor gradually loses its charge even inside a closed vessel. E. Rutherford and H. L. Cooke, and J. C. McLennan and E. F. Burton found a penetrating radiation in the lower atm., presumably derived from radioactive substances near the surface of the earth. J. Elster and H. Geitel showed that a bare wire exposed to the atm. and negatively charged, gradually becomes coated with a radioactive deposit which H. A. Bumstead showed to consist of varying proportions of emanations derived from radium and thorium. They can be collected from atm. air, (i) by absorption on charcoal; (ii) by condensation at a temp. below $-150°$; or (iii) by deposition on a conductor charged to a high negative potential. A. S. Eve estimated that an amount of emanation corresponding with 80×10^{-12} grms. radium per cubic metre of atm. air, and J. Satterly gave 100×10^{-12} grms. of radium per cubic metre. G. C. Ashman found the variations from day to day range from 45×10^{-12} to 200×10^{-12} grms. per cubic metre; A. S. Eve found the variation to be 1 to 7. Over the Pacific ocean and near the Antarctic ocean, the average amounts are respectively $3{\cdot}3\times10^{-12}$ and $0{\cdot}4\times10^{-12}$ grms. per cubic metre. Thus, the emanations are found more particularly in the atm. over land than over the sea. These emanations are more abundant in mines and cellars than in open air, and they are assumed to be derived by diffusion from the radioactive matters in the earth, and this is in agreement with the fact that the radioactivity of deep-sea water is greater near the bottom than near the surface. F. Henrich investigated the radioactivity of the gases from various springs—Gastein, Carlsbad, and Wiesbaden—and found them more radioactive than the spring water. The radioactivity of gases from thermal springs has been studied by P. Curie and A. Laborde, H. Mache, A. Herrmann and F. Pesendorfer, C. Moureu, etc. R. Nasini and co-workers, and E. Sarasin studied the radioactive gases from Tuscan suffioni; and J. Elster and H. Geitel, the gases from deep borings. In 1905, P. Langevin discovered the presence of a comparatively small number of slow-moving massive ions in the atm.; they are more abundant in towns

than in the open country. H. Kolhörster also found the existence of an extremely penetrating radiation in the atm. A part of this radiation is supposed to be derived from the earth because it decreases with elevation up to about 1·5 kilometres; but, from this level up to 9 kilometres, as far as it has been tested, the ionization increases very rapidly. It is therefore inferred that these penetrating radiations come from outside—apparently the sun.

C. T. R. Wilson [12] found that radioactive matter is carried down from the air by rain; and he isolated therefrom a radioactive preparation. The radioactivity of freshly fallen snow was established by S. J. Allen, J. C. McLennan, C. T. R. Wilson, H. A. Bumstead, A. Righi, G. Constanzo and C. Negro, etc., and a radioactive preparation isolated. According to J. Jaufmann, snow contains radium and thorium emanations. Ground-ice is also radioactive. F. Himstedt and J. C. McLennan, found fresh petroleum is very radioactive in virtue of a dissolved radioactive emanation; but that which has been distilled was found by E. F. Burton to be no longer radioactive. H. Mache and S. Meyer, G. Gehlhoff, and G. Severin and A. Hurmuzescu have studied the radioactivity of deposits and sediments from spring waters.

Cosmic particles found on the floor of the ocean have been examined by J. Joly [13] to find if radium occurs in extra-terrestrial regions; but he found no marked evidence of radium therein. None of the well-defined spectral lines of radium has been identified in H. A. Rowland's measurements of the solar spectral lines. F. W. Dyson reported that there are a few indecisive lines in the spectrum of the solar chromosphere which might belong to radium. H. Giebeler detected radium and its emanation in the spectrum of the star Nova geminorum 2; and M. B. Snyder also reported radium in the spectra of spiral nebulæ and of star clusters. H. Bongards believes a radium emanation to be a minor component of the solar material rays.

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§ 4. The Properties of Becquerel's Rays

The Becquerel rays from pitchblende have the same properties as the radiations from radium; they produce similar effects, but the latter act over a million times more intensely than the former. Radium radiations ionize the air through which they pass, and, as J. Elster and H. Geitel [1] have shown, the electrical discharge passes more freely through the ionized air; brush and spark discharges pass into a glow discharge. P. Curie,[2] A. Righi, H. Becquerel, G. Jaffé, C. Böhm-Wendt and E. von Schweidler, H. J. van der Bijl, T. Bialobjesky, H. Greinacher, J. C. McLennan and D. A. Keys, A. Zaroubine, etc., found that many liquid insulators acquire to a greater or less degree the power of conducting electricity when exposed to the influence of radium radiations; this is the case, for instance, with carbon disulphide, petroleum ether, carbon tetrachloride, benzene, liquid air, vaseline, amylene, paraffin, etc. B. Sabat found that the conductivity of highly purified water is not appreciably affected by β- and γ-rays; but F. Kohlrausch found the conductivity is augmented $0{\cdot}01\times10^{-6}$ times by the action of radium radiations. The ionization of solid dielectrics by Becquerel's rays was found by H. Becquerel, and demonstrated by A. Righi, T. Bialobjesky, B. Hodgson, W. Dietrich, A. Schaposchnikoff, and H. Greinacher. According to A. Becker, shellac, mica, and rubber become conducting under the influence of these rays; the conductivity of selenium was found by F. Himstedt, and E. Bloch to be augmented; B. Sabat, and R. Paillot found that the resistance of copper, iron, bismuth, platinum, steel, and brass is augmented by exposure to these rays, and it diminishes when the rays are removed. J. Trowbridge and W. Rollins detected no influence on aluminium. N. Hesebus studied the action of radium radiations on contact electricity; and N. Georgiewsky, on the speed of cooling of a hot body. J. J. Thomson found that, like cathode rays, and ultra-violet light, radium radiations in air sat. with moisture cause the condensation of water.

M. S. Curie [3] found that preparations rich in radium salts glow with a faint blue **phosphorescence**; the greater the degree of purity of the preparation, the more intense the luminescence. W. Marckwald concluded that the luminescence decreases as the degree of purity increases; he said that highly purified radium bromide has but a feeble luminescence. *Au contraire*, O. Hönigschmid said that molten purified radium chloride or bromide luminesces so strongly that it can be seen in daylight as a faint violet-blue glow. S. Meyer and E. von Schweidler found that cooling to the temp. of liquid air has no influence on the luminescence. M. S. Curie observed that the colour of the phosphorescent light becomes more violet with the lapse of time. The luminescence does not always disappear immediately the source of the rays is removed. H. Rüchardt and G. Berndt observed the action of α-rays from radium on phosphorescent strontium bismuth phosphide. H. Herszfinkiel and L. Wertenstein studied the tracks of the α-particles which make a grazing impact on a zinc sulphide screen.

E. Marsden found the luminescence with a sample of **zinc blende**, exposed to radium radiations, attained a maximum after 20 minutes' exposure, and vanished rather more slowly when the exciter was removed; with **willemite** the maximum

is quickly attained and it likewise quickly vanishes. S. Meyer and K. Przibram observed the after-luminescence persisted for some hours with certain samples of **fluorspar, kunzite,** and **Iceland spar.** F. Giesel said that the action with anhydrous radium halide is decreased when water is present, but the intensity is restored when the preparations are dried. Soln. luminesce faintly, although it is difficult to distinguish between the luminescence of the soln. and of the walls of the containing vessel.

H. Becquerel, P. and M. S. Curie, F. Giesel, P. Bary, G. T. Beilby, J. Borgmann, etc., noted the intense luminescence produced by radium radiations on adularia (blue), apatite (green to orange), barium cyanoplatinate (green), calcite (rose), cerussite (blue), colemanite (blue), diamonds (blue), fluorspar (blue), fowlerite (blue), greenockite (blue), Iceland spar (rose), kunzite (red to orange), magnesium cyanoplatinate, millerite (green to orange), native sulphur (blue), orthoclase (blue), pectolite (orange), quartz (blue), rhodonite (blue), rock-salt (blue), sapphire (blue), scheelite (blue), sparteite (orange), uranyl sulphate, willemite, wollastonite (orange), zinc blende (yellow), zircon (blue), etc. Less intense is the luminescence with amblygonite, amethyst, analcime, anglesite, anhydrite, apophyllite, aragonite, autunite, barytes, beryllonite, bertrandite, brewsterite, brucite, capholite, castor, chabasite, cœlestine, edllingtonite, gypsum, harmotome, heulandite, jamesonite, kainite, lanarkite, leadhillite, linarite, mimetesite, montebrasite, natrolite, opal, potash alum, prehnite, pyromorphite, quartz (smoky), ruby, scolecite, sericite, serpentine, sodium nitrate, spodumene, stilbite, strontianite, tourmaline, thenardite, witherite, zincite, zircon. Among other luminescent substances are salicylamide, and salicylates of zinc and the alkaline earths; salts of quinine; carbon disulphide; petroleum, glass, paper, gun-cotton, animal skin, blood, horn, nails, saliva, etc.

W. and M. L. Huggins found that the weak phosphorescent light of radium showed the band spectrum of nitrogen. This has been traced to the action of the α-rays, either in free nitrogen close to the radium, or in the nitrogen occluded in the radium compound. The violent collisions of the α-particles from radium with the molecules of the gas in its path set up vibrations which give the characteristic spectrum of the gas. This unusual result, says E. Rutherford, is the first example of a gas giving a spectrum when cold, without the stimulus of a strong electric discharge. B. Walter and R. Pohl found that the atoms of nitrogen appear to be more easily stimulated than those of any other gas yet examined. F. Himstedt and G. Meyer give 3577, 3371, 3300, and 3159 for the wave-lengths of the lines in the spectrum. W. Crookes, and J. Dewar and P. Curie said that the spectrum is not observed if the luminescent radium salt is confined in an evacuated vessel. J. Stark, W. Marckwald and K. Hermann have also discussed this subject.

Native substances which exhibit **thermo-luminescence** lose this quality when they have been heated a long time, but the property is restored by exposure to radium radiations or to cathode X-rays. Thus, W. Trenkle restored marble and apatite; H. Becquerel, fluorspar; G. Kunz and C. Baskerville, chlorophane; and S. Meyer and K. Przibram, kunzite, fluorspar, and Iceland spar. Some substances which do not exhibit thermo-luminescence, acquire this quality after exposure to radium radiations—*e.g.* browned glass; and quartz. Various borates also show thermo-luminescence after exposure to radium radiations, or cathode rays.

Li	Na or Ba	Be	Mg	Sn	Zn or Zr	Ni	Cr or Mn
reddish-orange	green	orange-yellow	ruby-red	blue	white	rose	yellow

M. S. and P. Curie [4] noted that when **glass** and **porcelain** are exposed to radium radiations, they are coloured violet or brown; the coloration depends on the composition; glass containing manganese appears violet. The discoloration persists after the source is removed, but if heated to 500°, the original colour is restored and the change is attended by thermo-luminescence. The action has been discussed by M. S. Curie, R. Lucas, W. Crookes, S. C. Lind, N. Georgiewsky, etc. Didymium glass, according to C. Baskerville, becomes **rose-coloured.** Many **minerals are discoloured** by exposure to radium radiations.

A. Miethe found numerous gem-stones are discoloured by radium radiations—diamond, sapphire, emerald, chrysoberyl, topaz, tourmaline, etc. Dark-coloured sapphires, ruby,

and dark-coloured tourmalines are not changed. The action of radium radiations on different minerals and salts has been studied by E. Goldstein, F. Giesel, S. Skinner, W. Ackroyd, etc.—molten quartz becomes dark brown; rose quartz, smoky quartz, and citrine become dark brown; topaz becomes orange-yellow; amethyst, darker violet, sapphire, brownish-yellow; ruby, deeper in colour; Iceland spar, citron-yellow; and zircon, reddish-brown. Hiddenite and willemite are scarcely changed; kunzite becomes green; fluorspar, violet; bakelite, wine-red; barytes, blue; barium cyanoplatinate, yellowish-brown; zinc sulphide, yellow; hemimorphite, brownish-yellow; hyacinth, reddens; sulphur, greenish-yellow; rock-salt, blue; mercurous sulphate, brown; and potassium uranyl sulphate, yellow; etc. The action on some salts of the alkalies and alkaline earths is shown in Table II.

TABLE II.—ACTION OF RADIUM RADIATIONS ON SALTS OF THE ALKALIES AND ALKALINE EARTHS.

	Li	Na	K	Rb	Cs	Ca	Sr	Ba
Chloride	violet to brown	yellow	purple	bluish-green	green	rose yellow	—	—
Bromide	yellow to grey	lilac	sky blue	—	—	—	—	—
Iodide	brownish-yellow	yellow	greenish-blue	—	—	—	—	—
Sulphide	—	greenish-blue	—	—	—	—	—	—
Sulphite	—	greyish-violet	—	—	—	—	—	—
Sulphate	bluish-grey	greyish-violet	greenish-blue	—	—	—	lilac	greenish-brown
Carbonate	white	lilac	greenish-lilac	blue	—	—	—	—
Borate	reddish-brown	violet	blue	greenish-blue	—	yellowish-brown	dark brown	dark grey
Phosphate	—	rose-violet	—	—	—	—	—	rose
Silicate	—	topaz-yellow	blue	—	—	—	—	—

The theory of the discoloration of minerals by the action of radium radiations has been studied by J. Elster and H. Geitel, R. Abegg, F. Giesel, E. Wiedemann and G. C. Schmidt, E. Bose, etc.—*vide* **2.** 20, 15. H. Siedentopf found that with the ultramicroscope, particles of sodium could be detected in discolored sodium chloride. F. Goldstein found the discoloration is more intense if the substance has been previously heated or melted. F. Giesel found the colours may be different if impurities are present. J. Elster and H. Geitel found that when the discoloration vanishes, the decolorized salt is photoelectric in daylight. N. Georgiewsky found that mica shows chromatic polarization changes which disappear with heat; while gypsum and Iceland spar change their optical properties but are not discoloured. N. Egoroff, and C. J. Salomonsen and G. Dreyer found colourless quartz becomes pleochroic. P. Lenard and S. Saeland, and S. Meyer and K. Przibram observed the photoelectric effect with discoloured kunzite, fluorspar, etc. W. Crookes found that the diamond is partially graphitized.

According to M. S. Curie,[5] the effect of radium radiations on a photographic plate is similar to that of light. The **photographic action** has been studied by J. Petri, G. W. A. Kahlbaum, C. Bonacin, S. Skinner, U. Behn, H. Stroud, S. Kinoshita and H. Ikeuti, M. Reinganum, W. Michl, E. Rutherford and H. Geiger, E. Mühlestein, S. Meyer and F. Paneth, W. Makower and H. P. Walmsley, R. R. Sahni, F. Mayer, etc.

The formation of ozone by the action of α-rays outside a thin glass bulb containing some emanation, or in the neighbourhood of a conc. radium preparation, can be detected by its odour. F. Krüger also found ozone to be formed by cathode

rays. In either case the ozonization is considered to be an electrical process—in the former case by α-rays, in the latter by β-rays. R. A. Millikan and co-workers showed that the ionization of some common gases—*e.g.* oxygen—by α-rays results in the removal of one electron per mol. S. C. Lind assumed a cluster of ions are formed about a charged atom or molecule, which, on being electrically neutralized, would break down into the highest stable polymer—ozone in the case of oxygen. L. B. Loeb, and E. M. Wellisch doubt the formation of cluster-ions. The mechanism of the ozonization of oxygen has been discussed by W. W. Strong, and E. K. Rideal and J. Kunz; while the formation of triatomic hydrogen has been investigated by G. L. Wendt and R. S. Landauer. P. and S. Curie, and F. Giesel found that **air** and **oxygen** are ozonized by radium radiations. According to S. C. Lind, the radiations from a gram of radium form 0·72 grm. ozone per hour.

According to S. C. Lind, *the chemical activity of the α- or β-rays is to be attributed to their kinetic energy and ionizing power, not to their own charges, which, in comparison with the secondary charges produced, are wholly insignificant.* In nearly all the reactions brought about by the α-rays, there is an approximate statistical agreement between the number of ions generated, and the number of molecules acted upon. F. Giesel and G. Bodländer, and W. Ramsay and F. Soddy found that the **water** in which a radium salt is dissolved is decomposed, forming hydrogen and oxygen—and, according to W. Ramsay, the α-rays are the agent which evokes the decomposition. W. Ramsay and A. T. Cameron showed that the rate of the reaction is proportional to the quantity of emanation present; and that each atom of emanation as it disintegrates produces the same amount of chemical action. Conversely, W. Ramsay observed that a gram of radium gives 32 c.c. of the detonating gas in 100 hrs. A 5 per cent. excess of hydrogen is produced—he said that the excess is not explained by the oxygen having oxidized something, nor is it probable that the excess hydrogen is produced by the decomposition of radium itself. It is thought that the first stage of the reaction involves the formation of hydrogen peroxide: $2H_2O=H_2+H_2O_2$. According to F. L. Usher, a gram-atom of emanation decomposes about 154,000 mols of water. The subject has been studied by A. Debierne, W. Duane and O. Scheuer, C. Runge and G. Bodländer, K. Bergwitz, F. L. Usher, A. T. Cameron, M. Kernbaum, H. B. Baker, K. von Körösy, etc. Owing to the decomposition of water by radium preparations, the preservation of moist samples in sealed tubes may end in the bursting of the tube. A sealed tube with dry samples should have a piece of platinum wire sealed in the wall to dissipate the accumulating positive charge. B. Davis and C. W. Edwards, A. T. Cameron and W. Ramsay, O. Scheuer, and S. C. Lind found that with a mixture of **hydrogen and oxygen gases,** some water is formed—*q.v.*—and A. T. Cameron and W. Ramsay and W. Duane and O. Scheuer noted that water vapour is but slightly decomposed by the α-rays, $2H_2O=2H_2+O_2$. They also noted the decomposition of ice. H. J. H. Fenton showed that the speed of the decomposition of **hydrogen dioxide** is accelerated by radium radiations to twice the normal speed. M. Kernbaum showed that the amount of hydrogen peroxide formed in water is eq. to the deficiency of oxygen in the gaseous product. He said that the penetrating radiations result in the exclusive formation of hydrogen peroxide and hydrogen. M. S. Curie, A. Kailan, and M. Kernbaum made estimates of the energy utilized in these reactions.

S. C. Lind found that **hydrogen and bromine** unite to form hydrogen bromide when exposed to α-rays. The reverse reaction, the decomposition of **hydrogen bromide,** $2HBr=Br_2+H_2$, also occurs. A. T. Cameron and W. Ramsay noted the decomposition of **hydrogen chloride,** while M. Bodenstein, H. S. Taylor, and W. P. Jorissen and W. C. Ringer found that the reaction between **hydrogen and chlorine**—*q.v.*—is accelerated by radium radiations, but they noted no such effect with hydrogen and oxygen. Although a mixture of hydrogen and chlorine unites under the influence of radium radiations, hydrogen chloride, hydrogen bromide, and **hydrogen iodide** are decomposed. These reactions have been investigated by A. Kailan, M. S. Curie, W. Ramsay and A. T. Cameron, F. Giesel, J. Pinnow,

H. J. M. Creighton and A. S. Mackenzie, H. S. Taylor. F. Giesel observed that **barium chloride** which contains some radium chloride is spontaneously decomposed, and some chlorine is given off; similarly with the bromides—ozone and barium oxide are formed; some chlorate or bromate may also be produced. In aq. soln., F. Giesel noted that, owing to the action of the liberated bromine on barium hydroxide, some hypobromite is formed. F. L. Usher studied the decomposition of **ammonia** by radium emanation. The reaction was attributed to the β-particles. E. E. Wourtzel, and S. C. Lind also investigated the reaction. No definite evidence of the formation of ammonia from a mixture of hydrogen and nitrogen was observed. E. E. Wourtzel investigated the decomposition of **hydrogen sulphide,** and of **carbon dioxide;** the last-named reaction and the decomposition of **carbon monoxide** were also investigated by A. T. Cameron and W. Ramsay. E. E. Wourtzel found that **nitrous oxide** is decomposed, $N_2O=N_2+O$, or $N_2O=N+NO$. G. H. Henderson found that **nitrogen iodide** is exploded when bombarded by radium radiations 3 or 4 cms. distant. The result is the same when all but the α-rays are screened.

P. Curie and A. Debierne, D. Berthelot, F. Giesel, L. Frischauer, etc., have indicated a number of chemical changes produced by radium radiations. Thus, monoclinic **sulphur** is changed into the rhombic form, and the velocity of crystallization of the sulphur is affected. Red amorphous **selenium** is crystallized, and the conductivity is affected in the same manner as it is by light, but to a smaller extent. In the presence of moist radium salts, the surface of **platinum** is blackened owing to the formation of a film of oxide. H. Becquerel found that yellow **phosphorus** becomes red; D. Berthelot, that **nitric acid** gives nitrous fumes, and **iodic acid** is decomposed; and G. Pellini and E. Vaccari made some observations on the last-named reaction. S. C. Lind observed a slight decomposition of **potassium iodide, lead iodide,** and **lead chloride** by the α-rays, while **lead bromide** was not decomposed. The valency of an element in its compounds is often reduced by radium radiations; thus H. Becquerel found **mercuric chloride** in the presence of oxalic acid forms mercurous chloride; and W. H. Ross, and A. Kailan noted the formation of ferrous from **ferric salts.** W. B. Hardy and G. Willcock found that soln. of **iodoform** in chloroform, carbon disulphide, or pyridine in darkness is coloured purple by radium radiations owing to the separation of iodine; the reaction was also studied by W. P. and W. E. Ringer. G. Pellini and E. Vaccari said that soln. of **propyl and isopropyl iodides** in iodoform are more strongly influenced by light than by radium radiations. G. Pellini and E. Vaccari did not observe any reaction between **uranyl nitrate** and oxalic acid, or between **sodium nitroprusside** and ferrous chloride under the influence of radium radiations while in darkness. According to V. Henri and A. Mayer, if a colloidal soln. of ferric hydroxide and silver be mixed with sodium acetate so that no colloid is precipitated, but, when exposed to the radium radiations, the positive colloidal **ferric hydroxide** is precipitated while the silver is not influenced. R. W. Lawson studied the disintegrating action of α- and β-rays on metals.

G. Schwarz found that under the influence of radium radiations, egg-shells are coloured brown; and F. Giesel, that paper is charred, and **celluloid** becomes brittle; J. B. Burke reported that **gelatine** is converted into turbid masses which appear to grow like living cells, but W. A. D. Rudge found that the effect is produced by the formation of insoluble sulphate from the sulphur dioxide contaminating the gelatine. G. Dreyer and O. Hanssen studied the coagulation of **albumen** by radium radiations; A. Fernau and W. Pauli, **proteins**—lecithin and cholesterol. W. B. Hardy noted that soln. of **globulin** change in colour and viscosity when exposed to Becquerel's or to α-rays. The action of these radiations on various **organic compounds** has been reported by J. J. Sudborough, Lord Blythswood, H. P. Martin and W. P. Morton, D. Berthelot, W. Ramsay and W. F. Cooke, P. Mesernitzky, O. Flaschner, H. Becquerel, A. Kailan, C. Doelter, W. P. Jorissen and W. E. Ringer, E. von Knaffl-Lenz and W. Wieckowsky. W. Caspari and

C. Neuberg, etc. **Vaseline** and **lubricants,** employed for stop-cocks and stoppers, may be changed into hard substances, and the cocks and stoppers are then moved with great difficulty ; **caoutchouc** becomes hard and brittle ; and **ebonite** is profoundly altered. A. Fernau studied the action of radium radiations on **sugar** and **agar-agar.** F. Sekera discussed the bearing of colloid chemistry on radioactivity.

According to F. Giesel,[6] if the eyes be closed, and a tube of radium bromide be held near the forehead, the retina of the eye becomes phosphorescent, and light will be seen though the eyes are closed. A tube containing a little radium bromide when held near the skin for a few hours produces painful sores. Caterpillars and other small animals are said to be killed if shut up in a box with a minute fragment of radium. It is also claimed that the exposure of malignant skin diseases, superficial cancer nodules, etc., has proved beneficial in many cases, although the testimony of medical experts is not unanimous.[7]

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§ 5. Analysis of the Radiations from Radium

The complexity of the radiations from radium is illustrated by the following facts: A few sheets of paper or a sheet of aluminium foil about 0·1 mm. thick will cut off a large part of the radiations, and a sheet of lead, about half a centimetre thick, will cut off nearly all the radiations. A residuum still remains unsuppressed even after passing through 15 cms. of lead or through a far thicker block of iron. Hence, **the radiations from radium are not homogeneous.** Again, the radiations from radium are not affected in the same way by a magnet. Some of the rays are not influenced, for they do not bend when placed in a magnetic field, these are called the γ-rays, these rays have the greatest penetrating power; others are bent *towards* the magnet, and are called the β-rays; while others are bent *away* from the magnet, and are called the α-rays; these rays have the least penetrating power. There are thus at least three distinct types of rays in the radiations emitted from radium salts:

1. Alpha rays.—The α-rays are slightly bent by intense magnetic forces.[1] The deviation is small and requires an intense magnetic field, so that at first the effect of the magnetic field on these rays was overlooked. E. Rutherford and co-workers, M. S. Curie, etc.,[2] have studied the behaviour of the α-rays in the electrostatic field. The results show that these rays carry a positive charge. **The general properties of the α-rays correspond with those of the canal rays in a vacuum tube.** The experimental evidence leads to the inference that the α-rays are streams of positively charged atoms projected from radium with a velocity approaching 20,000 miles per second. F. Giesel[3] showed that the impact of α-rays on Sidot's blende produces a scintillating effect which J. Elster and H. Geitel, and W. Crookes observed through a lens, and found to be compounded of a number of distinct flashes of light. The emission of α-particles from radium salts can be illustrated very neatly by **W. Crookes' spinthariscope.** A small fragment of a radium salt supported at the tip of a wire (Fig. 3), in front of a screen, coated on the inside with zinc blende, is viewed in the dark through a magnifying eyepiece, which is focussed on to the screen by sliding it up or down the tube. Flashes of light are continually scintillating on the screen. R. K. Duncan likens the effect to the appearance of a swarm of fireflies on a dark night. The scintillations are caused by the rain of α-particles from the radium salt on to the screen. Each impact is marked by a flash of light. E. Regener showed that each α-particle produces one flash. F. H. Glew observed a similar effect with the diamond in place of Sidot's blende. E. Rutherford and

H. Geiger devised a method of counting the α-particles based on this effect—*vide infra* for an analogous electrical method. The effects of the magnetic and electric fields on the motion of the α-rays have enabled their velocity and charge to be calculated. The earlier observations were made on non-homogeneous rays, and are therefore rougher approximations than the results of the latter work.[4] For the ratio e/m E. Rutherford obtained $6{\cdot}1\times10^3$, and for the velocity V, $2{\cdot}5\times10^9$ cms. per sec.; A. S. Mackenzie obtained respectively e/m, $4{\cdot}6\times10^3$, and $V=1{\cdot}3\times10^9$ to $2{\cdot}0\times10^9$ cms. per sec.; and T. Descoudres, e/m, $6{\cdot}4\times10^3$, and $V=1{\cdot}65\times10^9$ cms. per sec. The best representative value for e/m is $4{\cdot}8\times10^3$ electromagnetic units. According to E. Rutherford and H. Geiger, the charge e on a single α-particle is $9{\cdot}3\times10^{-10}$ electrostatic units; and E. Regener obtained $e=9{\cdot}58\times10^{-10}$ electrostatic units or $3{\cdot}18\times10^{-20}$ electromagnetic units. A quantum of energy according to the quantum theory is between $4{\cdot}65\times10^{-10}$ and $4{\cdot}77\times10^{-10}$ electrostatic units. Hence, the α-particles from radium have two such charges; and m varies from $6{\cdot}43\times10^{-24}$ grms. to $6{\cdot}59\times10^{-24}$ grms. The mass of a hydrogen atom is $1{\cdot}66\times10^{-24}$ grms. Hence, the mass of the α-particle is four times that of the hydrogen atom. It is therefore inferred that the α-particles are atoms of helium, each carrying two positive charges. This conclusion was confirmed by direct experiment—*vide infra*, Fig. 4. The kinetic energy of an ejected α-particle is about $5{\cdot}9\times10^{-6}$ ergs. The total kinetic energy of the α-rays can be calculated from the number n of particles emitted by a gram of radium per hour, the mass, m, of the α-particle, and the velocity V since the total kinetic energy is then $\frac{1}{2}nmV^2$.

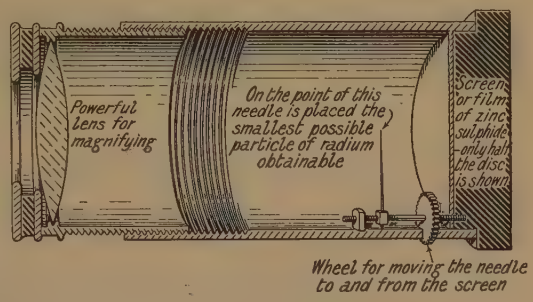
Powerful Lens for magnifying
On the point of this needle is placed the smallest possible particle of radium obtainable
Screen or film of zinc sulphide - only half the disc is shown
Wheel for moving the needle to and from the screen

FIG. 3.—Spinthariscope.

E. Rutherford and H. Geiger devised an electrical method for **counting the α-particles emitted by radium.** A small disc with a little emanation was fixed to a

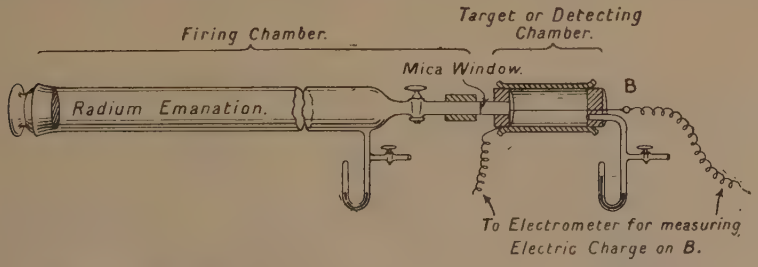

FIG. 4.—Apparatus for counting the α-particles emitted by radium emanation. (After E. Rutherford and H. Geiger.)

small iron cylinder and placed in a long glass cylinder—Fig. 4. The position of the radium disc could be adjusted by means of a magnet. This chamber—called the *firing chamber*—had a small mica window opening into a brass cylinder with ebonite ends and fitted with a central wire, B, connected with an electrometer. The brass cylinder was exhausted, and it then forms the target or *detecting chamber*. It was found possible to adjust the conditions so that two to five particles per minute passed through the mica window and upset the electrical equilibrium of the testing chamber. Each particle signalled its arrival by an unmistakable jump of the needle of the electrometer. The needle can be arranged so that its movements are recorded on

a chart (Fig. 5). Each jump represents the arrival of one particle in the " detecting chamber." Some of the jumps show that two particles sometimes arrive simultaneously or almost simultaneously. Given the size of the window and the distance of the source of the projectiles, simple arithmetic furnishes the number shot per minute in all directions from the radium emanation. The results were consistent with those obtained by counting the number of scintillations produced per minute when a zinc sulphide screen was used as a target, and show that about $3{\cdot}4\times10^{10}$ to $3{\cdot}57\times10^{10}$ of **α-particles are shot per second from a gram of radium.** Each α-particle passes into one atom of helium—*vide infra.*

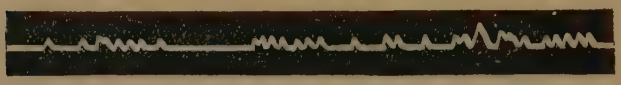

Fig. 5.—Chart showing movements of the needle of the electrometer on the arrival of α-particles.

The path of the ray through a moist gas has been made visible, owing to the condensation of water about the ions produced in the track of each α-particle. C. T. R. Wilson [5] has photographed the fog so produced in the tracks of the α-particles, and the photographs make it very plain that the ionizing power of the particles rapidly reaches a maximum, and then rapidly sinks to zero as they pass into molecules of helium. In general, the tracks of the α-particles are straight lines, but in some cases there is an abrupt bend near the end of their ranges. It is supposed that this is due to the particle being deflected from its course as its speed is slackening because it encounters the nucleus of another molecule. It is assumed that the α-particle passes through all the atoms it meets, and in doing so loses kinetic energy because (i) the track is a straight line, and (ii) it cannot push the atoms it encounters out of its way because these atoms are heavier than itself, and it meets with hundreds of thousands. In ordinary molecular motions, two atoms are said to collide when their centres are so far from each other that the free path is extremely short—about 10^{-5} cms. The immense speed of the α-particle accounts for the difference in the two types of encounter. One atom cannot be penetrated by another when the mutual velocities are small, say, 10^5 cms. per sec.; but when these velocities are, say, ten thousand times greater, the atoms are not impenetrable. In the latter case, the kinetic energy is so great that intense forces are necessary to deflect the particles. When an α-particle happens to pass close to the nucleus of an atom with a large positive charge, the path will be deflected, and the rays scattered; the nearer the particle passes to the nucleus, the greater the deflection. On the assumption that the electric force about the nucleus varies according to the inverse square law, E. Rutherford showed that the α-particle will describe a hyperbolic orbit about the nucleus, Fig. 3 (**3.** 27, 3). The career of the α-particles has been investigated at different stages of its flight. At the beginning, when the speed and kinetic energy are greatest, the particle does *least* work in ionization. It is supposed that just as a swiftly speeding bullet can cut a clean hole in a pane of glass, while a slowly moving bullet will shatter the glass, so when the speed of the α-particles is greatest, they can pass right through the molecules of a gas without producing any appreciable effect; but towards the end of their flight the ionizing power is greater because of the greater shattering power of the slowly moving particles; and finally the particle ceases to ionize the gas and settles down to " ordinary life " as a helium molecule (or atom). The movement of the swiftly speeding α-particles is obstructed as they pass through a gas. The damping action of different media on speed of the α-rays is comparatively large, so that these rays have a low penetrative power. According to E. Rutherford and H. T. Brooks,[6] they do not pass plates of mica or glass 0·1 mm. thick, nor plates of aluminium 0·05 mm. thick. Working with aluminium sheets 0·0034 mm. thick, and measuring the penetration of the α-rays by the ionization produced in air:

No. of plates of Al	0	1	2	3	4	5	6	7
Ionization	100	48	23	13·6	6·4	2·5	0·9	0

The maximum range of the α-particles is a characteristic of the parent substance. The velocity of the α-particle gradually decreases, but after the particle has travelled a certain distance the effects produced—ionization, scintillations, and photographic activity—cease abruptly. This distance is called the range of the α-particle in air. It is inversely proportional to the density of the air. The range of the α-particles in air ejected from radium is 3·00 cms., and the velocity $1{\cdot}50 \times 10^9$ cms. per sec. If the introduction of a medium reduces the range to 2 cms., the stopping power of the medium is said to be eq. to 1 cm. of air. From the weight per unit area of the medium, say gold sheet, it is possible to calculate the number of atoms of gold through which the α-particles have passed, and the stopping power of the gold atom can be compared with that of the average air atom. H. R. von Traubenberg measured the range of the α-rays in solids. When expressed in 10^{-4} cms. units of length, the results are :

Li	Cu	Ag	Au	Ca	Mg	Zn	Cd	Al	Tl	Sn	Pb	Fe	Ni	Pt
129·1	18·3	19·2	14·0	78·2	57·8	22·8	24·2	40·6	23·3	29·4	24·1	18·7	18·4	12·8

and he represented the results by means of a formula involving at. wt., at. number, range, and sp. gr. K. Heil studied the effect of α-particles on crystals.

The stopping power, S, of a gaseous medium for the α-rays is determined, not by the physical or chemical properties of the gas, but solely by its molecular weight. In general, *the stopping power of an element is nearly proportional to the sq. root of at. wt.* This is the case whether a gas like hydrogen or a metal like gold is involved, and is shown by the results in Table III, due to W. H. Bragg. The at. wt. is the one quality of importance. The stopping power is not only independent of the physical

TABLE III.—STOPPING POWER OF DIFFERENT ELEMENTS FOR THE α-RAYS.

Element.	S	$SA^{\frac{1}{2}}$.	Element.	S	$SA^{\frac{1}{2}}$.
Hydrogen	0·24	0·240	Nickel	2·44	0·319
Carbon	0·85	0·246	Copper	2·46	0·309
Nitrogen	0·94	0·251	Bromine	2·50	0·291
Oxygen	1·05	0·262	Silver	3·28	0·316
Aluminium	1·495	0·287	Tin	3·56	0·326
Sulphur	1·76	0·312	Platinum	4·14	0·297
Chlorine	1·78	0·299	Gold	4·22	0·301
Iron	2·29	0·307	Lead	4·27	0·298

state of an element, but it is also independent of the presence of neighbouring molecules. Chemical association is of no importance. J. L. Glasson formulates the stopping$=0{\cdot}262N^{\frac{2}{3}}$, where N is the at. number. W. H. Bragg and W. T. Cooke showed that the additive rule is applicable to chemical compounds, *the stopping power of a molecule is proportional to the sum of the at. wt. of the contained atoms.* Thus,

	O_2	CO_2	CO	C_2H_2	C_2H_4	C_2H_6	CH_4
Observed	1553	2187	1437	1619	1906	2180	1242
Calculated	1540	2200	1435	1618	1906	2194	1241

The stopping power is not altogether independent of the speed of the particle since the value of the constant is not the same for α-rays obtained in different rays, and of different speeds. W. Bothe discussed the scattering of the α-rays. P. Lenard and co-workers, A. Rüttenauer, and J. Königsberger have discussed the general equations for the velocity of particles in gases.

The kinetic energy of the α-particles passing through a gas is expended in doing work. The gas into which the α-particles are discharged becomes a conductor of electricity, and it acquires a greater chemical activity. The gas is said to be ionized. The relative degrees of ionization produced in a number of gases and vapours by the α-particles from radium have been studied by E. Rutherford,[7] W. H. Bragg,

R. J. Strutt, T. H. Laby, R. D. Kleemann, etc. Representing the effect with air unity, the values with the hydrogen halides are 1·29, and with

N_2	O_2	H_2	CO	CO_2	NH_3	CH_4	C_2H_2	C_6H_6	C_5H_{12}
0·96	1·08	1·98	1·01	1·01	0·95	1·17	1·26	1·29	1·35

Excepting hydrogen, the ionization produced in gases by the α-rays is approximately proportional to the densities of the gases.

E. Rutherford, and W. H. Bragg showed that if r denotes the range of the α-particles yet to be completed, their velocity $V=k(r+a)^{\frac{1}{2}}$, where k and a are constants; and the former found that, as indicated above, the α-particle completes its range with much of its energy still unspent. H. Geiger represented the velocity by $V^3=kr$, where k is a constant; and if i denotes the ionization, r the range to be completed, $i^3=a/r$, where a is a constant. This curve—dotted line, Fig. 6—follows observations fairly closely. The rate at which energy is spent is proportional to VdV/dT, and therefore to $r^{-\frac{1}{2}}$ and to the ionization; so that ionization is proportional to the energy spent. Since the product iV is a constant, it follows that ionization is proportional to the time the α-particle spends within the atom; and also that *ionization is a consequence of the presence of an α-particle within the atom, and depends for its amount on the time taken by the α-particle to cross the atom.* The α-particles can travel but a few cms. before their initial velocity is exhausted, and they pass by de-electrification into ordinary molecules of helium. In air, for instance, H. Geiger, and W. H. Bragg found that the α-particles from uranium are slowest, and they can travel about 2·58 cms. at 0° and 760 mm. or 2·75 cms. at 20° and 760 mm., while those from radium gave a range of 3·13 cms. at 0° and 760 mm. or 3·36 at 20° and 760 mm. R. A. Millikan and co-workers showed that the velocity of the α-rays from radium is a different order from that employed by J. J. Thomson for positive-ray analysis (*q.v.*). G. H. Henderson found that the observed straggling of the α-particles is greater than that deduced from the present theory of the passage of α-particles through matter.

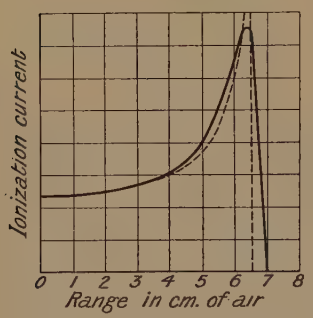

Fig. 6.—Variation of Ionization in the Track of a Pencil of α-rays.

2. Beta rays.—The β-rays are readily bent by comparatively weak magnetic forces in the opposite direction to the α-rays; and they carry a negative charge.[8] **The general properties of the β-rays correspond with those of the cathode rays of the vacuum tube,** for they appear to be negatively charged electrons or corpuscles projected from the radium salt with a velocity approaching 100,000 miles per second. The corpuscles in Crookes' tube travel a little faster than the β-rays from radium. A difference in speed might be expected from their different modes of generation.

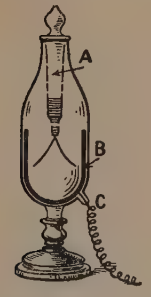

Fig. 7.—Strutt's Radium Clock.

The following experiment—**R. J. Strutt's radium clock**—illustrates the character of the β-rays. A morsel of a radium salt is enclosed in a glass tube, *A*, Fig. 7, coated with a conducting material and ending at the bottom with a brass cap from which hang a pair of gold leaves. This system is fitted within a glass tube from which the air is exhausted. The inside of the tube is coated with strips of tinfoil, *B*, connected with the earth by the wire, *C*. The β-rays from the radium pass through the glass and leave the central system with a positive charge. This causes the gold leaves to diverge gradually until they touch the tinfoil, when they are discharged, and the leaves collapse. The process begins anew. This charge and discharge goes on continuously since the radium can emit these radiations an indefinitely long time. This arrangement is perhaps the nearest approach yet made to perpetual motion. The frequency of the cycle, of course, depends upon the amount of radium in the inner tube.

The β-rays are not homogeneous, but have widely different velocities; similar remarks apply to the value of the ratio e/m. On the assumption that the charge remains constant, this means that the mass m is not constant. W. Kaufmann showed that if m_0 be the mass of a particle at rest, and m the mass when its velocity is a fraction β of the velocity of light, $m=m_0(1-\beta^2)^{-\frac{1}{2}}$. For $\beta=\frac{1}{2}$, $m=1{\cdot}15m_0$, and for $\beta=0{\cdot}9$, $m=2{\cdot}3m_0$. For low velocities, $m=m_0$, and $e/m=1{\cdot}77\times10^7$ electromagnetic units, or $5{\cdot}31\times10^{17}$ electrostatic units; and $m_0=\frac{1}{1834}$ (oxygen=16). In absolute units, $m_0=0{\cdot}876\times10^{-27}$ grms., and $e=4{\cdot}65\times10^{-10}$ electrostatic units. R. A. Millikan gave $m_0=0{\cdot}898\times10^{-27}$ grms., and $e=4{\cdot}77\times10^{-10}$ electrostatic units. These give respectively $1{\cdot}83\times10^{-13}$ cms. and $2{\cdot}00\times10^{-13}$ cms. for the radius of the particles. F. Lerch discussed the effect of chemical treatment on the β-ray activity of radium.

The distribution of the β-rays of different velocity has been investigated by deflecting them in a magnetic field, and focussing the deflected rays on to a photographic plate. A homogeneous beam of β-rays produces a sharp band whose position enables the velocity to be calculated. Rays of lowest velocity are deflected most abruptly, and those of greatest velocity least abruptly. The result is the so-called *magnetic spectrum of the β-rays*. Usually, there are numerous sharp bands or lines on the photographic plate as well as a less intensely marked background which is continuous.

The passage of the β-particles through matter is not understood so clearly as in the case of the α-particles. It is not easy to get a homogeneous beam of β-rays. The velocity of the β-particles averages nearly ten times that of the α-particles, but the mass is so much less, that the momentum and kinetic energy of the β-particles are less than that of the α-particles. The kinetic energy of the α-rays is about 3·3 times that of the β-rays. Hence, the β-particles are more readily deflected in their encounters with atoms in their path. Instead of passing through matter in a straight line, the path is more or less tortuous. This is shown by C. T. R. Wilson's photographs [9] of the track of the β-rays in air; the photographs were obtained by a process analogous to that used for the α-rays—*vide supra*. If the β-ray moves rapidly it produces a straight track, but the slower-moving rays have more or less tortuous tracks, being deflected hither and thither by collision with the molecules of the gas. C. Ramsauer, and H. F. Mayer studied the cross-sectional area of gas molecules towards slow electrons.

The absorption of the β-rays by matter sometimes follows the simple exponential law $I=I_0e^{-kd}$, where I_0 denotes the ionization current without an absorbing screen; I, the current for a screen of thickness d, and k is the coeff. of absorption. The value of k depends to some extent on the observation apparatus, and also on the source generating the β-rays; with some rays, the absorption curve is only approximately exponential; in other cases it is additive, $I=I_1e^{k_1d}+I_2e^{-k_2d}+\ldots$ P. Lenard found the coeff. of absorption k for the cathode rays was approximately proportional to the sp. gr.; E. Rutherford found the law applied to the swifter β-rays from uranium; R. J. Strutt, for the complex β-rays of radium. E. Rutherford's results are shown in Table IV; the ratio k/D varies from 4·4 for carbon to 10·8 for lead. The plotting of the ratio k/D with the at. wt. shows that the variations in the values of this ratio are in harmony with the periodic rule. J. A. Crowther, H. W. Schmidt, etc., found that the ratio k/D follows the additive rule, so that if M be the mol. wt. of a compound, and A_1, A_2, ... the at. wt. of the constituent atoms, $Mk/D=\Sigma(Ak/D)$. The range of the β-particles was measured by W. H. Bragg, G. A. Sutherland and L. H. Lamb, etc. The scattering of β-rays has been studied by H. Geiger and W. Bothe, J. A. Crowther and B. F. J. Schonland, etc. The β-ray spectrum has been investigated by L. Meitner, C. D. Ellis, and A. Smekal. The ionization of gases by β-rays has been studied by P. Lenard,[10] W. Wilson, etc.

J. J. Thomson [11] found that matter traversed by α-rays furnishes a number of secondary radiations which he called *delta-rays*, or δ-rays. It has been proved that the delta-radiation is produced by slow-speed negative electrons which are large in number compared with the α-particles.

TABLE IV.—ABSORPTION OF β-RAYS BY ELEMENTS OF DIFFERENT DENSITY.

Element.	At. wt.	$\frac{k}{D}$	Element.	At. wt.	$\frac{k}{D}$	Element.	At. wt.	$\frac{k}{D}$
B	11	4·65	Cr	52	6·25	Ag	108	8·3
C	12	4·4	Fe	56	6·4	Sn	118	9·46
Na	23	4·95	Co	59	6·48	Sb	120	9·8
Mg	24·4	5·1	Cu	63·3	6·8	Tl	126	10·8
Al	27	5·26	Zn	65·5	6·95	I	126	10·8
Si	28	5·5	As	75	8·2	Ba	137	8·8
P	31	6·1	Se	79	8·65	Pt	195	9·4
S	32	6·6	Sr	87·5	8·3	Au	197	9·5
K	39	6·53	Zr	90·7	8·0	Pb	207	10·8
Ca	40	6·47	Pd	106	8·0	U	240	10·1
Ti	48	6·2						

From Isaac Newton's principle of action and reaction, it follows that when a particle of mass m and velocity v is ejected from an atom of mass M, the residual atom of mass $M-m$ must recoil with a velocity V such that $(M-m)V=mv$. The momentum of an α-particle is much greater than that of a β-particle, so that the velocity of recoil for the expulsion of an α-particle will be greater than for expulsion of a β-particle. The **recoil atoms** carry a positive charge, and they can be collected in a negatively charged plate. This enables a separation of some mixtures of radioactive substances to be made.[12]

3. Gamma rays.—The γ-rays are not affected by the most intense electric and magnetic forces.[13] The γ-rays do not appear to be material particles at all; the experimental evidence shows that **the γ-rays are similar to, if not identical with, Röntgen rays.** The chief difference is that the γ-rays are usually more penetrating than the X-rays, and they have a shorter wave-length. A diagrammatic illustration of the three types of radiation from radium is given in Fig. 8. A piece of radium is supposed to be placed in a lead vessel, *A*, sufficiently thick to prevent rays travelling through the walls. Under the influence of an intense magnetic field, the rays no longer travel in straight lines, but they are deflected, as shown diagrammatically in the figure. It will be observed that the α-rays and β-rays are alone corpuscular; the γ-rays are analogous with light rays of very small wave-length. Their penetrative power is very intense, and they can manifest their presence after passing through several inches of metallic lead or several feet of metallic iron.[14] K. W. F. Kohlrausch studied the secondary radiations produced when the γ-rays act on matter. The relative penetrative powers of the three types of rays for aluminium are roughly as $\alpha:\beta:\gamma=10:10^3:10^5$. The passage of γ-rays and of X-rays through matter is a complex phenomenon which has not been elucidated. It involves the production of secondary X-rays (*q.v.*). C. T. R. Wilson found that the tracks produced by the Röntgen rays closely resemble those produced by the β-rays, and it is presumed that the Röntgen or γ-rays excite β-rays in matter on which they fall, and that the effects produced by the γ-rays are directly due to the β-rays to which they give birth. The ionization of media through which the γ-rays are passing, has been studied by H. Prelinger, V. F. Hess, W. H. Bragg, R. D. Kleeman,[15] etc. L. de Broglie studied the conditions of equilibrium between atoms, electrons, and radiation in an enclosure at a constant temp.

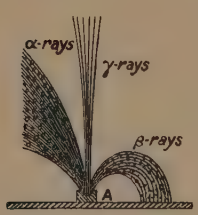

FIG. 8. — Diagrammatic Analysis of the Radium Radiations by a Magnet.

The impact of cathode rays on matter gives rise to X-rays; and β-rays also behave similarly. It is therefore inferred that the γ-rays from radium are produced by the β-rays as they escape from the atom. The γ-rays produced by different radioactive substances differ greatly in amount and in penetrating power.

E. Rutherford explains this by assuming that the tracks of the β-particles from the nuclei of the different atoms outwards are differently related with the surrounding electronic rings. If the β-particle passes through a region in the atom where there are feeble forces, a weak pulse of the γ-radiation will be produced; whereas if the β-particle travels along a certain critical path within the atom and sets into vibration a ring of electrons, there is a considerable loss of energy which reappears as a γ-radiation of a wave-length characteristic of the disturbed rings of electrons. This explains the grouping of the magnetic spectrum of the β-rays. The continuous magnetic spectrum is supposed to be produced by the γ-rays ejecting β-particles of definite intensity from the atom. L. Meitner, and A. Smekal discussed the relation between the β- and γ-rays.

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§ 6. The Properties of Radium

Radioactivity is the least manageable of natural processes. It will not be hurried or controlled. Nature keeps the management of this particular department in her own hands. Man views the phenomenon with hungry eyes, but his interference is barred out. He can only look on in wonder while it deploys its irresistible unknown forces.—ANON. (1907).

According to M. S. Curie and A. Debierne,[1] radium is a brilliant white metal; it blackens immediately on exposure to air, possibly owing to the formation of the nitride. A particle of the metal blackens white paper as if the latter had been charred. By extrapolation from the sp. gr. of calcium, strontium, and barium, the **specific gravity** of radium is nearly 6·0. The **melting point** is sharp at 700°. Radium is more volatile than barium; and it may be possible to separate the two elements by sublimation.

P. Curie and A. Laborde found that there is a continuous **emission of heat** from radium, so that the temp. of the element and its salts is always a little—about 1·5°—above the temp. of its surroundings. According to M. S. Curie, freshly prepared radium salts, solid or in soln., develop relatively little heat; but as time goes on, more and more heat is developed until, after about a month, the rate of development of heat assumes a stationary state. K. Angström observed that the rate of production of heat remained constant during seven months' observations. The month's period of induction, so to speak, has been traced to the development of certain more or less transient products of the disintegration of radium, which are themselves radioactive. In the stationary state, the rates of formation and dissipation are balanced. P. Curie and A. Laborde found that a gram of radium generates about 100 cals. of heat per hour; P. Curie and J. Dewar obtained a similar result; C. Runge and J. Precht gave 105 cals.; J. Precht, 113 cals., and later 134·4 cals.; F. Paschen, 126 cals.; E. Rutherford and H. T. Barnes, 110 cals.; K. Angström, 117 cals.; E. von Schweidler and V. F. Hess, 118 cals.; W. Duane, 120 cals., and later 104 to 117 cals.; and H. Petterson, 116·4 cals. J. Dewar found a slightly greater amount of heat to be developed in liquid hydrogen than in liquid oxygen or carbon dioxide.

P. Curie, and E. Rutherford, showed that the quantity of heat developed is but little affected by the external conditions. K. Angström found that neither an electric field nor a magnetic field makes any appreciable difference.

Normally, one gram of radium appears to evolve enough energy to raise a little more than its own weight of water from f.p. to b.p. every hour; this amount of heat is eq. to 118 cals. per hour, or about 1000 Cals. per annum. It has been estimated that a gram of radium will continue radioactive for about 2500 years, and it therefore follows that a gram of radium gives energy eq. to $5{\cdot}5 \times 10^8$ cals., or to that obtained by burning $\frac{9}{10}$ths of a ton of coal during the period of radioactive change. In other words, radium furnishes 250,000 times as much energy as is given by burning an equal weight of coal; or, as G. le Bon expressed it:

> Matter, formerly regarded as inert and only able to give back energy originally supplied to it, is, on the other hand, a colossal reservoir of energy—infra-atomic energy—which it can expend without borrowing anything from without.

Much of the atomic energy of the radium atom is transformed into kinetic energy as the α-, β-, and γ-rays are ejected; the energy of the recoil appears as heat. The radium which has stood for some time contains other products, *vide infra*, and taking all these things into consideration, E. Rutherford and many co-workers find that the kinetic energy of the α-rays is $1{\cdot}28 \times 10^6$ ergs per sec., or 110 cals. per hr.; that of the recoil action, 2·04 cals. per hr.; that of the β-rays is 3·8 per cent. of that of the α-rays or 4·18 cals. per hr., and that of the γ-rays is 5·2 per cent. of the α-rays or 5·72 cals. per hr., making a total of 122 cals. per hr. for a gram of radium in equilibrium with its disintegration products as far as radium C. The phosphorescence of radium was shown by W. Duane to have no perceptible influence on the development of heat—*vide* radium emanation.

Hence, **radium is continually doing work at an undiminishing speed without any external supply of energy;** otherwise expressed, the reaction is exothermal. Whence comes this supply of energy? How does the continuous evolution of heat by radium agree with the dogma that heat cannot come from nothing, but must come from some other source? The heat of a stove is derived from the oxidation of the fuel inside; with radium, it is assumed that the atoms (or molecules) are continually changing. If radium be an element, and the radium atoms are changing into something not radium, it follows that there must be some flaw in the hitherto universally accepted conception of an element.

W. H. Bragg and R. D. Kleeman,[2] H. Geiger and J. M. Nuttall, and E. Rutherford give for the **range of the α-particles** of radium in air at normal press. 3·13 cms. at 0° and 3·30 cms. at 15°; the **velocity** in air at $15° = 1{\cdot}6 \times 10^9$ cms. per sec.; the **momentum,** $0{\cdot}987 \times 10^{-14}$; the **kinetic energy,** $0{\cdot}794 \times 10^{-5}$ ergs; and the **number of ions** produced by the absorption of an α-particle by air, $1{\cdot}50 \times 10^5$. The **radioactive constant,** γ—*vide infra*—is 0·000346 (year). E. Rutherford and H. Geiger estimated the **average life-period** of radium at 2500 yrs.; and the **half-life period** at 1760 yrs. (*vide infra*); B. B. Boltwood gave respectively 2880 and 2000 yrs., which are the best representative values, and B. Keetmann gave 1800 yrs. for the half-life period. The **parent** of radium is ionium (*q.v.*); the offspring, radium emanation (or niton) and helium. The nearest analogue is barium. When radium is freed from its emanation (*q.v.*) by heating it emits only α-rays and feeble β-rays, but no γ-rays. The α-ray activity of freshly prepared radium is but 20 per cent. of that which is exhibited by old preparations—*vide infra* radium emanation. O. von Bäyer and co-workers found that there are two groups of **β-rays** with the respective velocities 0·52 and 0·65 in terms of the velocity of light. O. Hahn and L. Meitner, and L. Kolowrat observed that the **absorption coefficient of the β-rays** in terms of cms. of aluminium is 200.

The emission of the corpuscular radiations from radium and its compounds naturally suggests that the element is continually losing weight A. Heydweiler[3] reported that 5 grms. of a strongly radioactive preparation regularly lost 0·02 mgrm.

every 24 hrs.; but E. Dorn observed that 2·9 mgrms. of purified radium bromide did not lose 0·001 mgrm. in three months' time; and he showed that precautions must be taken against electrostatic effects in weighing preparations of radium. W. Wien, assuming that $6{\cdot}6\times10^{9}$ β-particles are lost from a gram of radium bromide per second, estimates a loss of $1{\cdot}2\times10^{-10}$ grms. per annum; and if 10^{11} α-particles are lost per second, there will be a further loss of 6×10^{-6} grms. per annum.

F. Giesel [4] found that radium salts impart a carmine-red colour to Bunsen's flame. If this flame be coloured by barium bromide, and a trace of radium bromide be introduced, the barium spectrum, particularly in the red, is masked. The **flame spectrum** of radium consists of lines and bands. There is a fine red band between wave-lengths 4700 and 6530, in which occurs a prominent line at 6653; there are orange-yellow lines at 6349, 6329, 6285, 6269, 6247, and 6210; a strong orange-yellow band between 6330 and 6130, and a feeble one between 6050 and 5900; a strong blue line at 4826; feeble blue lines at 4750, 4718, 4680 (possibly 4682), and 4595; and a feeble violet line at 4405. C. Runge and J. Precht observed these and other lines. It is not known whether the bands belong to the metal or to the bromide. E. Demarçay examined the **spark spectrum** of impure radium chloride first prepared by its discoverer, and he afterwards examined a specimen of a higher degree of purity. The spark spectrum has been examined by C. Runge and J. Precht, A. Miethe, F. Exner and E. Haschek, etc. The chief lines in the spark spectrum are 5813 in the yellow; 5660, 5616, 5601, 5556, 5502, 5406, 5400, 5319, 5097 in the green; 4856, 4826, 4682, and 4641 in the blue; and 4533, 4436, and 4340 in the violet; of these lines, only 4826 and 4682 appear in the flame spectrum. E. Demarçay found two bands in the spark spectrum of the chloride—one between 4621·9 and 4631·0, and the other between 4463·7 and 4453·4. These bands have not been observed by later observers, and it is therefore possible that they belong to the chloride. W. and M. L. Huggins studied the spectrum of phosphorescing radium. The **ultra-violet spectrum** has been examined by F. Exner and E. Haschek, G. Berndt, and W. Crookes; and the **arc-spectrum** by F. Exner and E. Haschek. The **Zeeman effect** has been observed by C. Runge and J. Precht. The spectral lines of the magnesium-calcium family can be grouped in three pairs; and the stronger lines of the radium spectrum are analogous with the stronger lines of the spectra of the other elements of the same family. The two lines of each of the three pairs are the same distance apart for any one element, but the distances apart of the lines in passing from one element to another increase in a regular manner with increasing at. wt. Thus:

	Magnesium.	Calcium.	Strontium.	Barium.	Radium.
At. wt. . . .	24·36	40·1	87·6	137·4	?
Distance . .	91·7	223	801	1691	4858·6 units.

By plotting the at. wt. as functions of the distances between the lines, extrapolation furnished C. Runge and J. Precht, G. Rudorf, and W. M. Watts an approximate value for the at. wt. of radium. The extrapolation is easier if logarithms of the at. wt. and the distances apart of the lines be plotted. The graph for a group of chemically related elements then lies in a straight line, as indicated in Fig. 9. The series spectra of radium have been studied by W. Ritz, W. M. Hicks, E. Fues, and A. Fowler.

P. Curie and C. Chéneveau [5] found the **magnetic susceptibility** of radium chloride to be $+1{\cdot}05\times10^{-6}$, so that the element is feebly paramagnetic in combination. Barium is diamagnetic, $-0{\cdot}40\times10^{-6}$; hence, observations on samples contaminated with barium are very unreliable. M. S. Curie found a mixture of barium chloride with 17 per cent. of radium chloride to have a magnetic susceptibility of $-0{\cdot}20\times10^{-6}$. S. Meyer, and P. Pascal have also made observations on this subject; and the latter found that the paramagnetism of radium occupies a position adjacent to the metals of the alkaline earths.

According to M. S. Curie and A. Debierne, radium decomposes water energetically and dissolves for the most part, showing that the oxide is soluble. M. S. Curie [6]

determined the **atomic weight** of radium. She found that 0·0919 grm. of the anhydrous chloride, whose spectrum showed the presence of barium but faintly, gave 0·0859 grm. of silver chloride. Hence, 0·0919 grm. of radium chloride contains 0·0213 grm. of chlorine; or 35·46 grms. of chlorine unite with 117·5 grms. of radium. Hence, the eq. of radium is 117·5. If radium chloride be $RaCl_2$, by analogy with barium chloride, $BaCl_2$, the at. wt. of radium is nearly 235. The bivalency of radium was confirmed by the diffusion experiments of G. von Hevesy on the assumption that the diffusion coeff. of the cation of radium chloride is represented by $1{\cdot}25n^{-1}$ sq. cm. per day, where n denotes the valency; and H. Freundlich and G. von Elissafoff's observations on the electric endosmose phenomenon, where the vol. of liquid transported plotted with the conc. of the soln., gave curves in agreement with bivalent barium and magnesium salts, but not with sodium or aluminium. Later determinations by M. S. Curie, with purer materials and in larger quantities, gave 226·35; T. E. Thorpe, by a similar process, obtained 226·58; R. W. Gray and W. Ramsay, 226·36; and O. Hönigschmid, $225{\cdot}97 \pm 0{\cdot}012$. The value obtained by C. Runge and J. Precht,[7] from spectral observations, was 258, Fig. 9.

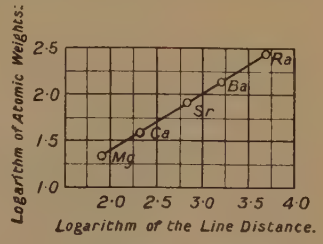

FIG. 9.—Relation between the Atomic Weights and the Distance apart of the Spectral Lines of the Calcium-Radium Family of Elements.

The salts of radium.—M. S. Curie[8] said that radium is a higher homologue than barium in the alkaline earth family, and it stands in the same vertical column as the alkaline earths, and in the same horizontal period as the radioactive elements thorium and uranium. It is very similar in its analytical properties to barium; and R. de Forcrand places it in the electrochemical series between sodium and barium: Cs, Rb, K, Na, Ra, Ba, Sr, Li, Ca, . . . By extrapolation, he computed values for the heats of formation, solubilities, and heats of reaction of the halides, and the oxide. P. Lemay and L. Jaloustre found radium salts act as catalysts in some oxidation processes. Radium **chloride** and **bromide** are less soluble in water or in the corresponding haloid acids than the salts of barium. C. E. Scholl noted the formation of the complex salt $RaBr_2.2BaBr_2.6H_2O$ in acid soln. Radium **carbonate** and **sulphate** are also less soluble than the analogous barium salts, so that radium sulphate is considered to be less soluble than any other known sulphate. S. C. Lind and co-workers measured the solubility of radium sulphate and found that if a soln. mixed with barium sulphate be precipitated by adding a soluble sulphate, the ratio of barium to radium in precipitate and soln. is the same. The salts are not isotopic, and the phenomenon is therefore called *pseudoisotopy*. With radium sulphate alone, the mean value obtained for the solubility in water at 25° is $2{\cdot}1 \times 10^{-8}$ grms. per c.c., which is about one-hundredth of the solubility of barium sulphate. The presence of sulphuric acid up to 50 per cent. has no appreciable influence on the solubility. At higher acid conc., the solubility increases rapidly, the data obtained showing that the solubility is more than twelve times as great in 70 per cent. as in 60 per cent. acid. With $\frac{1}{10}N$-sodium sulphate the solubility increases to $12{\cdot}0 \times 10^{-8}$ grms. per c.c. In dil. acid soln. the solubility increases about 50 per cent. when the temp. is raised from 25° to 35°, and the same increase is found when the temp. is raised to 45°. The observed value of the solubility of radium sulphate is in agreement with that expected from a comparison of the solubilities of the sulphates of calcium, strontium, and barium. There is very little difference in the solubilities of the nitrates of radium and barium. The chloride, bromide, nitrate, carbonate, and sulphate were prepared by M. S. Curie.

Radium bromide and chloride crystallize with two mols of water of crystallization which is lost at 100°, according to M. S. Curie—O. Hönigschmid said below 200°. According to the latter, radium chloride melts at a dull red heat without decomposition. L. Kolowrat found that radium chloride melts at about 1000°, and there

is a transition point between 830° and 920°. M. S. Curie found that molten radium chloride freezes to a glassy mass. The vitreous chloride glows with a bluish-violet light visible in daylight; in a darkened room, the phosphorescent light is so bright that the time can be read from a watch 20 cms. away. The vitreous salt glows more strongly than the salt dried at 200°. According to C. J. Joly, radium bromide melts at 728°, and if heated to 1600°, an insoluble glassy residue remains. According to F. Rinne, dihydrated radium and barium chlorides are isomorphous; both crystallize in the monoclinic system; the barium salt has the axial ratios $a:b:c=1{\cdot}4494:1:1{\cdot}1656$, and the radium salt $a:b:c=1{\cdot}4485:1:1{\cdot}1749$. M. S. Curie found that the crystals of radiferous barium chloride assume a yellow or rose tint some hours after they have been prepared; the intensity of the colour depends on the relative proportions of the two chlorides. The presence of barium appears to be necessary because highly purified crystals of radium chloride are not so discoloured. F. Kohlrausch and F. Henning measured the electrical conductivity, λ, of soln. of radium bromide, and on the assumption that the at. wt. of radium is 225, and the formula of the salt, $RaBr_2.2H_2O$, obtained for soln. with N-gram-eq. per litre:

N- . .	0·05	0·02	0·01	0·005	0·002	0·001	0·0005	0·0002	0·0001
λ . .	99·4	105·7	110·0	113·4	117·1	119·4	120·9	122·7	123·7

he also determined the temp. coeff. of the conductivity and found 0·0221 at 18° for soln. with 1·024 per cent. of $RaBr_2.2H_2O$, and 0·0225 for 0·0286 per cent. soln. The ionic mobilities of the family of elements were Ca, 51·8; Sr, 51·7; Ba, 55·5; and Ra, 58. Electric endosmose phenomena of soln. of radium salts have been studied by H. Freundlich and G. von Elissafoff; and the diffusion of radium salts in soln., by G. von Hevesy. E. Ebler, and H. Herschfinkel prepared radium **azide,** $Ra(N_3)_2$, and found it behaves like the azides of the alkaline earths, decomposing into the metal and nitrogen between 180° and 250°. For the chemical properties of radium and its salts, *vide supra*, radium radiations.

According to W. Ramsay, a sample of radium bromide, $RaBr_2.2H_2O$, lost water and some bromine when kept in a sealed tube for some time. O. Hönigschmid found when the anhydrous chloride had been kept for two years in a quartz tube, the containing vessel showed numerous fine cracks, and hence quartz is not suitable for keeping radium preparations. Glass tubes with a platinum wire sealed in the walls to dissipate the electric charge are best suited for preserving samples of radium salts. The electric charge which a vessel acquires may be considerable. E. Dorn and M. S. Curie noted such tubes may give sparks when cut with a file; and J. Precht, and P. L. Mercanton obtained explosions with radium preparations in tubes. According to G. Denigès, barium and radium salts can be distinguished microchemically since they give distinct and definite salts with iodic acid, providing the conc. of the salt soln. does not exceed 0·3 per cent.

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§ 7. Radium Emanation—Niton

R. B. Owens [1] observed some irregularities in his measurements of the radioactivity of thorium compounds, which he traced to the action of currents of air, and E. Rutherford found that the effects were due to the emission of radioactive particles of some kind from the thorium compounds. This emanation is like a gas,

and it can be carried away by a stream of air: it can pass through a plug of cotton-wool, and be bubbled through soln. without losing its radioactivity. E. Dorn then showed that radium gives off a similar emanation. According to P. and M. S. Curie:

> Any substance placed in the neighbourhood of radium acquires a radioactivity which persists for many hours and even days after the removal of the radium. This induced radioactivity increases with the time during which it is exposed to the action of radium up to a certain limit. After the radium is removed, it decreases rapidly and tends to disappear. The kind of substance exposed to the radium is almost a matter of indifference, for all substances acquire a radioactivity of their own.

This induced radioactivity has been traced to the continuous evolution of a substance from radium which behaves as if it were a radioactive gas, and which is adsorbed by substances in its presence. In his early work, to avoid the hypothesis implied by calling the radioactive substance a gas, E. Rutherford, its discoverer, called it an *emanation*. R. W. Gray and W. Ramsay called the emanation from radium, **niton,** Nt—*nitens,* shining—in reference to the solid; W. Ramsay and J. N. Collie the emanation from radium *exradio;* that from thorium, *exthorio;* and that from actinium, *exactinio*. Chemists appear to prefer the term niton; physicists, emanation.

The emanation from radium is of almost universal occurrence; it is found in air, spring-water, river-water, sea-water, volcanic products, minerals, and rocks. The occurrence of radioactive substances has been discussed in connection with radium, and most of these refer to this emanation. The emanation is obtained from radium preparations which have stood for some time. Fresh preparations are usually free from the emanation. The preparation of the emanation has been described by E. Rutherford, and by W. Ramsay and co-workers. The emanation is expelled by melting the radium preparation, or by dissolving the preparation in a suitable solvent. The emanation can then be obtained by shaking, or boiling the soln., or pumping off the gases. The emanation decomposes water, and it will then be contaminated with detonating gas. This is removed by sparking; the organic matter derived from the lubricants of stopcocks is burnt by passing the emanation over heated lead dichromate and the carbon dioxide absorbed by soda-lime; the oxygen and hydrogen are removed by passing the gas over heated copper and cupric oxide; the moisture is removed by phosphoric oxide; and the nitrogen, by heated lithium. The emanation can also be frozen by liquid air and the hydrogen and oxygen pumped from the solid. According to W. Ramsay, if the frozen solid is red, it can be assumed that the emanation is of a high degree of purity.

If N_0 be the number of atoms initially present, and N the number remaining after an interval of time t, E. Rutherford showed that the velocity of decay dN/dt is proportional to the number, N, of atoms present, or

$$\frac{dN}{dt} = -\lambda N \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where λ is a constant; hence, the *law of decay is*

$$N = N_0 e^{-\lambda t} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the constant λ is invariable for a particular type of radioactive matter, but varies with different types of radioactive matter, and it has therefore been called the *radioactive constant*. Consequently, the law of radioactive change formally resembles the law of mass action. It is convenient to express the decay in terms of the so-called *half-life period*, that is, the interval required for the activity or the number of atoms present to fall to half value. Hence, $N = \frac{1}{2}N_0$, and $\frac{1}{2} = e^{-\lambda t}$, or $2 = e^{\lambda t}$, or $\log_e 2 = \lambda t$, or $\lambda t = 0{\cdot}69315\ldots$; consequently the half-life period, t, or the radioactive constant, λ, can be calculated when the other value is known. Again, the expression $N = N_0 e^{-\lambda t}$ means that any atom may exist unchanged for any time from zero to infinity; but after a time t, the number, dN, which changes in the time dt is equal to $\lambda N dt$, or to $\lambda N_0 e^{-\lambda t} dt$; but each of these atoms has a life t, so that the *average life* of the whole number is, by the laws of probability, $\int \lambda t e^{-\lambda t} dt$ between zero and infinity, *i.e.* λ^{-1}; or, the average life of an atom is the reciprocal of the radioactive constant. A. T. Cameron illustrates the meaning of the term average life employed in the study of radioactivity as follows: "If a church at a fixed time contains a number of people of different ages, then, given the number of years each person will live after leaving

the church, the average life of the congregation is reckoned from the time fixed by that church attendance." This is not the average life taken from the time of birth used in computing insurance rates.

The decay of the radium emanation is comparatively slow, measurements of the average life, and the half-life period have been made. P. Curie found 3·99 days for the half-life period, E. Rutherford and F. Soddy gave 3·71 days; A. Bumstead and L. P. Wheeler, 3·88 days; H. Mache and S. Meyer, 3·89 days; O. Sackur, 3·86 days; G. Rümelin, 3·75 days; M. S. Curie, 3·85 days; and E. Rutherford, 3·846 days. The best representative values of the decay constants in day, minute, and second units are:

	Days.	Hours.	Minutes.	Seconds.
Half-life period . .	3·85	$0·924 \times 10^{2}$	$5·55 \times 10^{3}$	$3·33 \times 10^{5}$
Average life . .	5·55	$1·330 \times 10^{2}$	$8·00 \times 10^{3}$	$4·80 \times 10^{5}$
Radioactive constant .	0·180	$7·50 \times 10^{-3}$	$1·25 \times 10^{-4}$	$2·085 \times 10^{-6}$

The products of the decomposition of the emanation of radium are (i) α-particles which, when the charges are neutralized, furnish helium gas; and (ii) a radioactive solid named radium A, which adheres to the surfaces of bodies. Radium A itself quickly undergoes a series of changes, so that the apparent product of the decomposition of radium emanation is a radioactive deposit which is a complex mixture included in the general term *active deposit*. The radioactivity produced on inactive bodies by a film of the active deposit is the cause of the *induced or excited radioactivity* discovered by P. and M. S. Curie in connection with radium, and by E. Rutherford in connection with thorium.

A genetic relationship between helium and the radioactive minerals was suspected by E. Rutherford and F. Soddy because helium is occluded in these minerals. W. Ramsay and F. Soddy found that when radium emanation is kept in a sealed glass tube, it shows the spectrum of helium, which gradually grows brighter as the emanation decays. One volume of the emanation furnishes roughly three vols. of helium. Further evidence in this connection was obtained by P. Curie and J. Dewar, T. Indrikson, F. Himstedt and S. Meyer, etc. Radium emanation thus decomposes into radium A and α-rays. E. Rutherford and T. Royds gave direct evidence that the accumulated α-particles consist of helium. They enclosed some radium emanation in a thin-walled glass tube surrounded by a vacuum jacket, Fig. 10. Each vessel was gastight; α-rays from the radium emanation could penetrate the walls of the inner vessel, but not the walls of the outer tube. By raising the left mercury reservoir, the gas in the annular space could be compressed in the spectrum tube, and there sparked, and examined spectroscopically. In two to six days' time, a gas with the spectrum of helium accumulated in the annular space between the two tubes. To show that the helium was not derived by diffusion from the inner tube, the emanation was removed and helium substituted. No trace of helium could be detected in the outer vessel after standing several days. This and other experiments have proved that the **radium passes into helium viâ the emanation.** Otherwise expressed, helium is one decomposition product of radium. Still further, the α-rays are streams of positively charged particles, and each particle carries two unit positive charges. **Radium emanation decomposes, continuously and spontaneously, into a radioactive solid and α-particles; each α-particle is an atom of helium carrying two unit positive charges.**

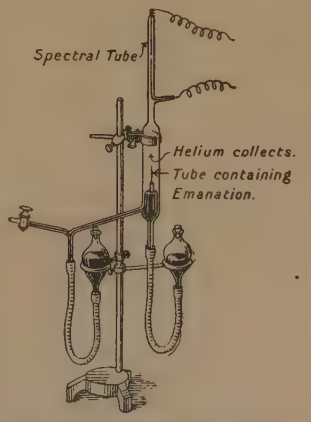

FIG. 10.—Rutherford's Experiment showing the change of α-particles into Helium.

Helium, said E. Rutherford, is not to be regarded as a decomposition product

of radium in the ordinary sense of the word ; rather is it a by-product derived from the emitted α-particles. **The production of helium is independent of the matter from which the α-particles have been derived.** A. Debierne observed the change with α-rays from actinium ; F. Soddy, from thorium and uranium minerals ; M. S. Curie and A. Debierne, and B. B. Boltwood and E. Rutherford, from polonium ; R. J. Strutt, from thorianite and pitchblende ; B. B. Boltwood, from ionium ; and E. Rutherford and B. B. Boltwood, from radiolead.

J. Dewar found a gram of radium, in equilibrium with the active deposit and emanation, furnished 169 c.mm. of helium at 0° and 760 mm. per annum. B. B. Boltwood and E. Rutherford obtained 156 c.mm. Assuming that each α-particle produces one helium atom, and that $3{\cdot}57\times10^{10}$ α-particles are emitted by a gram of radium, then, under the above conditions, where four emittors of α-particles are in equilibrium with radium, $14{\cdot}28\times10^{11}$ α-particles are emitted per second, and this is eq. to 162–167 c.mm. of helium per annum.

The rate of decay of radium emanation is quite independent of any known condition.—E. Rutherford found that it is independent of *concentration* or *pressure*, showing that it is not affected by the bombardment of its own radiations ; P. Curie found the rate to be independent of the *nature and pressure of surrounding gas ;* and he detected no difference whether the *temperature* be —180° or 450° ; E. Rutherford observed no difference in the rate at ordinary temp. and at the temp. of liquid air ; W. Makower and S. Russ obtained the same results at ordinary temp. and at 1100° ; E. P. Adams, F. Wallstabe, and R. B. Moore detected no difference when the emanation is *dissolved in water*, and F. Wallstabe, when *dissolved in toluene*. The fact that the rate of decay of the emanation is independent of physical and chemical conditions led P. Curie to suggest that the decay of the emanation could be employed to fix a standard of time.

E. Rutherford and F. Soddy showed that the emanation is singularly inert ; it is not affected by the mineral acids or by other liquid reagents, nor is it affected when heated to a high temp. with platinum, lead chromate, magnesium, etc. W. Ramsay and F. Soddy found that the emanation suffers no change when heated for an hour in the presence of a mixture of lime and magnesium ; it is not influenced by burning phosphorus ; nor by sparking a mixture of the emanation with oxygen over alkali-lye. J. J. Thomson, and F. Himstedt found that conc. acids, alkali-lye, red-hot copper or magnesium, the electric spark, and the silent electric discharge are without influence. Hence, said E. Rutherford, and W. Ramsay, radium emanation is chemically inert, and it behaves like a gas of the argon family.

The determination of the **atomic weight** of niton is difficult, because the available quantities are small, and because it is adsorbed by the containing vessel. If radium, at. wt. 226, is transformed into niton by the loss of an atom of helium, at. wt. 4, the at. wt. of niton should be near 222. R. W. Gray and W. Ramsay measured the **relative density** of about 0·001 mgrm. of niton, by means of a microbalance, sensitive to one-millionth of a mgrm. Assuming that niton is a monatomic gas, they obtained 227, 226, 225, 220, and 218—average, 223. These results are in accord with theory ; and show that niton is the heaviest gas known, being 111 times the density of hydrogen. The normal density was found to be 0·00996 when that of oxgyen is 0·001429. The at. wt. so determined is in agreement with diffusion and effusion methods of determining gas densities. E. Rutherford found 0·06 c.mm. of gaseous niton did not occupy in the liquid state more than $1{\cdot}2\times10^{-4}$ c.mm. Hence the **specific gravity** of the liquid is to that of the gas$=6\times10^{-2}/1{\cdot}2\times10^{-4}$ $=500$. R. W. Gray and W. Ramsay obtained 555. Hence the sp. gr. of the liquid, according to the former, is about 5, and, according to the latter, about 5·5.

E. Rutherford,[2] and W. Ramsay and co-workers found that niton follows Boyle's gas law. The constancy of the product pv, particularly for large volumes, is characteristic of permanent gases. When partially purified niton is forced into a capillary, there are marked changes in vol. during the first few hours, due to the chemical actions of the α-radiation from niton on the gaseous impurity ; the vol.

may expand or contract depending on the nature of the impurity; with purified niton the changes are less marked. After the initial changes, the vol. does not alter very much with time. The **compressibility** of niton between $p=0$ and $p=1$, is $-0{\cdot}019157$. R. W. Gray and W. Ramsay found the **vapour pressure,** p, to be

	−74·5°	−66·1°	−53·1°	−48·5°	−43·1°	−31·0°	−12·8°	+1·5°
p . .	100	200	500	760	1000	2000	5000	10,000 mm.

E. Rutherford gives 9 mm. at −127°; 50 mm. at −107°; 250 mm. at −78°; and 760 mm. at −65°. Niton behaves like ordinary gases, exhibiting a definite vap. press. for a definite temp. G. Rudorf found the values of f in J. H. van der Waals' formula, $\log p_c - \log p = f(T_c T^{-1} - 1)$, varied from 2·29 at 202·6° K. to 1·873 at 372° K.

A. O. Rankine found the coeff. of **viscosity** of the gas to be 0·0002130. E. Rutherford and H. T. Brooks, P. Curie and J. Danne, and L. Chaumont determined the coeff. of **diffusion** of niton gas in air, and found 0·1 sq. cm. per sec.; according to G. von Hevesy, this number is too high, and he considers the value is less than 0·07 sq. cm. per sec. at room temp. The diffusion constant obtained directly is too high for the at. wt. and T. Graham's rule. F. Wallstabe measured the diffusion of niton in water and in toluene, and found respectively 0·066 and 0·168 sq. cm. per day. E. Rona's value is 0·985 at 18° for water, and E. Ramstedt's value is 0·820. The last named also calculated the molecular diameter to be $1{\cdot}85 \times 10^{-8}$ cms. A. Debierne determined this **effusion** of the gas through a fine aperture; W. Makower compared the effusion with that of hydrogen, oxygen, carbon dioxide, and sulphur dioxide; and P. B. Perkins, with mercury vapour at 250°. The results are in rough accord with the observed at. wt.

The **specific heat** of niton has not been determined; for a monatomic gas of at. wt. 222–223, the at. ht. should be about 3; the sp. ht., $c_v=0{\cdot}0135$; $c_p=0{\cdot}0225$; and $c_p/c_v=1{\cdot}667$. Many of the effects ascribed to radium or radium-rays are really due to the occluded emanation, or to the active deposit produced by the decay of the emanation. Thus, E. Rutherford and H. Robinson analyzed the **emission of heat** in cals. per gram of radium:

	α-rays.	β-rays.	γ-rays.
Radium . .	25·1	—	—
Emanation . .	28·6	—	—
Active deposit .	69·9	4·7	6·4
Total . .	123·6	4·7	6·4 = 134·7

E. Rutherford and F. Soddy studied the temp. of condensation of niton to the liquid state in gaseous mixtures under low partial press. A. Laborde determined the temp. of condensation in spirals of copper, lead, silver, and glass; he obtained the same temp. for the metals −160° to −161·7°; but for glass, he obtained −164·4°. R. W. Boyle did not get so marked a difference for glass. P. Curie and J. Danne, J. J. Thomson, F. Himstedt, and H. Ebert condensed niton to a liquid by cooling in liquid air. R. W. Gray and W. Ramsay found the **boiling point** of niton to be −48·5°, but later gave −62°; E. Rutherford found −65°. R. W. Gray and W. Ramsay found the **melting point** to be −71°, at which temp. the vap. press. is still about 500 mm.—the solid is opaque and crystalline. Liquid niton undergoes a marked variation in colour as the temp. is lowered; at ordinary temp. the liquid is colourless and transparent. When cooled below the f.p., −71°, the condensed niton exhibits a brilliant phosphorescence, which becomes yellow as the temp. is lowered, and it appears orange-red at the temp. of liquid air; on raising the temp., the red phosphorescence becomes yellow at about −118°. These colours are complicated by the phosphorescence of the glass—in a quartz tube, the colour appears blue; in a soda-glass tube, lilac; and in a lead-potash-glass tube, bluish-green. R. W. Gray and W. Ramsay gave 104·5° for the **critical temperature,** and 47,450 mm. or 62·4 atm. for the **critical pressure.** G. Rudorf calculated the mol. **latent heat of vaporization** from W. Nernst's equation, $M\lambda = T(9{\cdot}5 \log T - 0{\cdot}009T)$,

and obtained for $T=211°$ K., 4387 Cals.; and from E. Clapeyron's equation, $M\lambda=3960$ Cals. Assuming that $M\lambda=3950$ and $M=222{\cdot}5$, the latent heat of vaporization is 17·75 Cals. per gram. G. N. Lewis and co-workers gave 41·81 for the **entropy** of niton at 25° and atm. press.

Radium emanation, or niton, emits only α-rays. W. H. Bragg and R. D. Kleeman,[3] H. Geiger and J. M. Nuttall, and E. Rutherford give for the **range of the α-particles** of niton in air at normal press., 3·94 cms. at 0°, and 4·16 cms. at 15°; **velocity** in air at 15°, $1{\cdot}73\times10^{9}$ cms. per sec.; the **momentum,** $1{\cdot}06\times10^{-14}$; the **kinetic energy,** $0{\cdot}915\times10^{-5}$ ergs; and the **number of ions** produced by the absorption of an α-particle by air, $1{\cdot}74\times10^{5}$. As previously indicated, the **radioactive constant,** λ, is 0·1800 day, or 0·0075 hr., or $2{\cdot}083\times10^{-6}$ sec.; W. Bothe and G. Lechner gave $\lambda=0{\cdot}1819$ day, or $2{\cdot}106\times10^{-6}$ sec.: the **half-life period** is 3·85 days; W. Bothe and G. Lechner gave 3·810 days; the **average-life period** is 5·55 days. The **parent** is radium, the offspring, radium A and helium, and the nearest analogue xenon. G. H. Briggs, and E. M. Wellish concluded that only a fractional part of the recoil atoms of radium emanation are positively charged at the end of their path; G. H. Henderson concluded that all are charged.

E. Rutherford observed a kind of relationship between the period of the transformation of a product and the velocity of the α-rays which it expelled. The greater the velocity of the α-rays, the shorter the period of the transformation. A relation is rendered evident by plotting the logarithms of the radioactive constants and the ranges, Fig. 11, of some decay products of uranium. H. Geiger and J. M. Nuttall represented the relation by $\log\lambda=a+b\log R$, where λ denotes the transformation constant; and R the range of the α-particles, while a and b are constants; H. A. Wilson gave $\log\lambda-\log R=a+bR^{\frac{1}{2}}$; R. Swinne gave $\log\lambda=a+bV^{n}$, where V denotes the velocity of the α-particle; a and b are constants; and $n=1$ or 2; and H. T. Wolff gave other expressions. E. Rutherford interprets these observations to mean that "the chance of an atom breaking up is greater, the greater the surplus energy to be got rid of to form the next product of the series." H. Geiger showed that in order that a radioactive substance may emit a particle of short range, say 1 cm., the period of transformation would be so long that the activity of the product would be too small to detect; and it corresponds with the fact that no known product emits α-particles of such short range. F. Kirchhoff has discussed this question.

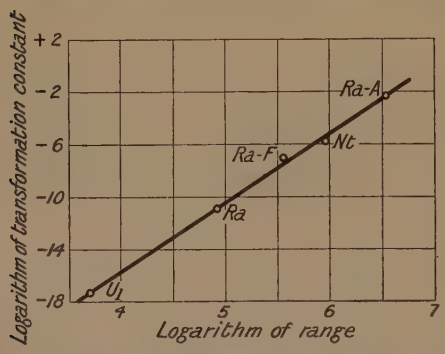

FIG. 11.—Relation between the Range and Life Period of the Decay Products of Uranium.

The **phosphorescent** effects produced by radium emanation have been discussed in connection with the properties of radium radiations. A. W. Porter and C. Cuthbertson[4] found the **index of refraction** of an impure sample of niton to be 1·000840; a sample further purified gave 1·000916; and it is inferred that the value would be 1·00092 with highly purified niton. The spark **spectrum** of niton is characteristic, and quite distinct from that of radium and of helium. The discharge in a tube of niton is bluish, and not so intense as that of a helium tube. The spark spectrum shows a group of strong green lines and another group of violet lines. W. Ramsay and J. N. Collie, and R. E. Nyswander and co-workers made some observations on this subject. E. Rutherford and T. Royds photographed the spectrum, and compared it with that of helium. Their results are shown in Fig. 12; the numbers represent wave-lengths. W. Ramsay and A. T. Cameron also published results derived from these photographs, but T. Royds showed that with the exception

of the more intense lines of niton, the spectrum coincided with that of xenon, and there thus appeared to have been an accidental and unsuspected contamination with xenon—W. Ramsay said *die einzige mogliche Erklarung ist dass unter gewissen Umstanden Niton in Xenon zerfällt!* H. E. Watson confirmed the results of E. Rutherford and T. Royds, and the last named found some additional lines in the ultra-violet. There is no clear evidence of the spectrum lines of niton in stellar spectra. The saturation current produced between two extended plate electrodes by radium emanation has been studied by L. Flamm and H. Mache.

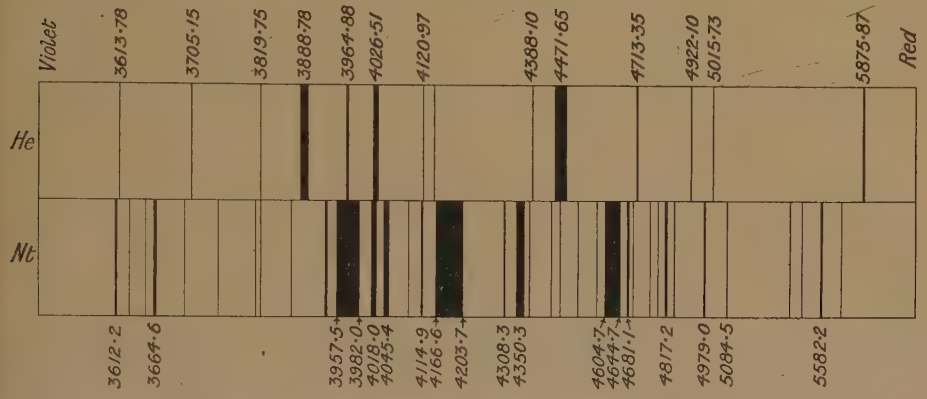

FIG. 12.—Spark Spectral Lines of Helium and Niton.

M. S. Curie [5] showed that water becomes radioactive by exposure to the emanations of radium, and this was ascribed to the absorption of the emanation by water. The discovery that well-water and spring-water contain much niton, but no radium, showed that the emanation must be soluble in water. Qualitative observations were made by P. Curie and A. Debierne, and F. Himstedt, R. Schenck and A. Schulze; while H. R. von Traubenberg, and H. Mache showed that **the solubility in water** resembles that of other gases. If a vol. v_1 of air or other gas, and a vol. v_2 of liquid be confined in a vessel; and when the system is in equilibrium, a vol. e_1 of niton be present in the gas, and a vol. e_2 be dissolved in the liquid; then, the conc. of niton in the gas is e_1/v_1, and in the liquid, e_2/v_2. The ratio of these conc. is a measure of the **absorption coefficient,** α, such that $\alpha=e_2v_1/e_1v_2$. H. R. von Traubenberg obtained $\alpha=0{\cdot}33$; and H. Mache, 0·32. R. Hofmann showed that the value of α decreased with temp.; and M. Kofler, that α decreased with increasing conc. of niton dissolved in the water. S. Meyer compared the observed values of α with those calculated from the relation $\alpha=0{\cdot}105+0{\cdot}405e^{-0{\cdot}0502\theta}$, and the results are:

	0°	5°	10°	20°	40°	60°	80°	100°
α (Obs.) . .	0·510	0·420	0·350	0·255	0·160	0·127	0·112	0·107
α (Calc.) . .	0·510	0·420	0·351	0·254	0·159	0·125	0·112	0·108

The agreement is excellent. The solubility formula $\alpha=a+be^{-c\theta}$ applies also to the gases argon, nitrogen, hydrogen, oxygen, carbon monoxide, and nitrogen monoxide, where the constant c has the same value. It is remarkable that at 100°, ten per cent. of niton remains dissolved in the water. R. W. Boyle found that the solubility decreases rapidly with temp., but for a definite temp., the coeff. is independent of the conc. of the gas, and also independent of the nature and press. of the inactive gas mixed with the niton. G. Jäger represented the solubility by the formula, $\alpha=e^{-W/RT}$, where W denotes the work which the surface forces perform in removing a mol at the absolute temp. T from the liquid into vapour, R is the gas constant. R. W. Boyle found for the heat of soln. Q cals., of niton in water:

	0°–5°	5°–10°	10°–15°	15°–20°	20°–25°	25°–30°	303–5°
Q . . .	6·7	6·3	5·8	5·6	5·5	5·1	4·7

H. Mache and S. Meyer, H. Sjögren and N. Sahlbom found values of α for a number of spring-waters; M. Kofler measured the absorption coeff., α, of niton in a number of salt soln., and found at 18° for soln. with the bracketed sp. gr., *mercuric chloride* (1·049), $\alpha=0·250$; *silver nitrate* (1·190), $\alpha=0·192$; *potassium permanganate* (1·038), $\alpha=0·194$; *ferrous sulphate* (1·226), $\alpha=0·081$; *ammonium chloride* (1·078), $\alpha=0·096$; *lead nitrate* (1·237), $\alpha=0·166$, and (1·283), $\alpha=0·143$; *potassium chlorate* (1·175), $\alpha=0·061$, and (1·028), $\alpha=0·187$; *potassium ferrocyanide* (1·107), $\alpha=0·102$; *zinc sulphate* (1·346), $\alpha=0·041$, and (1·199), $\alpha=0·092$; *cupric sulphate* (1·193), $\alpha=0·075$, and (1·042), $\alpha=0·194$; *sodium chloride* (1·203), $\alpha=0·042$, (1·008), $\alpha=0·239$; *sea-water* (1·028), $\alpha=0·165$; *sugar soln.* (1·214), $\alpha=0·114$, and (1·082), $\alpha=0·188$; and aq. soln. of *alcohol* (0·977), $\alpha=0·300$, and (0·800), $\alpha=5·606$. Eq. soln. of different salts have nearly the same coeff.; sodium chloride (1·0392), potassium chloride (1·0449), and cupric sulphate (1·0776) have the respective values $\alpha=0·165$, 0·163, and 0·157. R. W. Boyle also made observations with sea-water, and he found that the gas is virtually insoluble in *mercury*. R. Hofmann, A. Lurié, and E. Ramstedt referred the solubilities in some liquids to the formula $\alpha=a+bc^{-s\theta}$, when the temp. θ is expressed in hundredths of the interval between the m.p. and the b.p.; $a+b$ denotes the solubility at the m.p. Thus,

	m.p.	b.p.	a	b	c
Carbon disulphide	−110°	46·3°	13	900	0·054
Ethyl ether	−117·6°	34·6°	10	700	0·055
Toluene	−92·4°	110·7°	2	125	0·045
Chloroform	−63·2°	61·2°	9·5	90	0·043
Ethyl alcohol	−117·6°	78·4°	2·5	86	0·046
Acetone	−94·6°	56·1°	4	68	0·046
Ethyl acetate	−83·8°	77°	4	66	0·048
Xylene	−55°	139°	1	68	0·045

At temp. between 18° and 20°, α for *olive oil* and similar oils is 28; for *carbon disulphide*, 23; *cyclohexane*, 18; *hexane*, 17; *turpentine*, *ethyl ether*, *chloroform*, and *amyl acetate*, 15; *toluene*, *benzene*, and *xylene*, 13; *vaseline*, and *petroleum*, 10; *paraffin*, 9; *ethyl acetate*, 7·4; *acetone*, 6·3; *ethyl alcohol*, 6·2; *aniline*, 3·8; *glycerol*, 1·7; E. Ramstedt gives 0·21 for glycerol, and A. Lurié a higher value. G. Hofbauer found that with the homologous *alcohols* and *fatty acids*, the solubility increases as the CH_2-groups increase. H. Mache and E. Suess found for *blood*, $\alpha=0·42$; and E. Ramsauer and H. Holthusen, 0·31 at the body temp., 37°. A. Schulze also measured the solubility of niton in a number of organic liquids—toluene, ethyl ether, ethyl acetate, ethyl alcohol, chloroform, acetone, carbon disulphide, hexane, aniline, and benzene—at different temp.

The radioactivity which a substance acquires when exposed for some hours to niton is due to the deposition of a radioactive deposit which decays rapidly with time and becomes very small in about 12 hrs.; but P. Curie and J. Danne [6] showed that the acquired radioactivity of many solids—*caoutchouc*, *celluloid*, *wax*, *paraffin*, *meerschaum*, *platinum black*, *glass*, *alum*, *clays*, etc.—persists for many days. This was traced to the absorption or occlusion of the gas. The decrease is due partly to the decay of the emanation *in situ*, and partly to the escape of the occluded gas into the surrounding air. A similar effect was observed with some metals—*lead*, *platinum*, *aluminium*, *copper*, *bismuth*, and *silver*. L. Bunzl, E. Rutherford, A. S. Eve, J. Satterly, R. W. Boyle, and H. Mache and T. Rimmer have investigated the remarkably strong absorbent powers of *charcoal*, notably cocoa-nut charcoal, for radium emanation. G. von Hevesy found animal charcoal not as good. W. Mohr thus represented the percentages absorbed at different temp.:

−182°	−120°	−78°	−10°	0°	22°	100°	165°	250°	395°	490°
100	91·5	81·1	64·98	59·23	57·18	43·85	34·18	20·31	15·70	7·14

C. Porlezza and G. Norzi found that at −77° wood charcoal removes all the emanation from the gaseous exhalations of fumeroles; at −20°, about half is removed; and at 10° and higher temp., very little change occurs. E. Henriot observed that wood charcoal below 18° completely removes all the niton from an enclosed gas, while above 300°, virtually none is absorbed; between these temp., the quantity is a function of the temp. H. Herschfinkel found that admixtures of iron or uranium hydroxide, didymium fluoride, or iron chromate facilitate the expulsion of niton from radium. P. L. Mercanton found that niton does not diffuse through glass even when the latter is heated to its softening temp. The absorption is to a large extent dependent on the grain size of the material; the temp.; the amount of

moisture present; etc. E. Ebler and M. Fellner found colloidal substances—silicic acid, arsenic sulphide, and organic colloids—hold the emanation very tenaciously. The action has been studied by K. Horovitz and F. Paneth. Many metal salts occlude radium emanation; the oxides, hydroxides, chlorides, and bromides are more active than the carbonates or sulphates. M. S. Curie and A. Debierne, E. Rutherford, B. B. Boltwood, S. Meyer and V. F. Hess, and H. Holthusen have studied the occlusion of niton by solids.

Ordinary radium compounds in the solid form allow very little emanation to escape at ordinary temp., so that the greater part remains occluded with the parent. There is no evidence that the emanation is chemically combined with the radium; neither radium nor radiferous barium absorb any marked proportion of the emanation which has been released. The liberation of niton is facilitated by a rise of temp., the process is one of diffusion, and is facilitated by decreasing the grain-size of the material. As previously indicated, the occluded niton is liberated by fusing the material, or by dissolving it. M. S. Curie showed that both methods yield the same amount of niton for a given weight of radium. Dihydrated radium chloride loses its niton below the m.p., but when the water of crystallization has been expelled, a higher temp. is needed to drive off the niton. L. Kolowrat found that the amount of niton liberated from radium preparations depends not only on the temp. but on the time of heating. With anhydrous radium chloride, the effect of temp. is very slight up to 300°–400° and but little niton is lost; there is then a very rapid increase in the rate at which niton escapes up to 830°; above this the rate of escape decreases to a minimum at about 920°; and the rate then increases up to the temp. of fusion, about 1000°, when the whole emanation is given off. The fall in the rate of evolution of niton between 830° and 920° is connected with a change in the physical state of the salt. The loss of niton at a given point on the time-temp. curve is independent of the total amount accumulated in the body. The fact that the emanation can be driven off from radium with a greater velocity as the temp. is raised has no reference to the statement that radioactive processes are independent of the physical conditions, because the emanation is already there. The rate at which the radium manufactures the emanation is not affected by temp., etc.

Starting with a radium preparation freed from the emanation, and confined in a sealed vessel to prevent the loss of the small fraction which might otherwise escape by diffusion, if q atoms of niton are produced per second, and N atoms of niton be present at the time t, λN particles of niton change every second, where λ is the so-called radioactive constant. Then, dN, or $q-\lambda N$, particles of niton will be produced in the time, dt, so that the rate at which the niton accumulates in the system is equal to their rate of production less their rate of change, or

$$\frac{dN}{dt}=q-\lambda N \quad . \quad . \quad . \quad . \quad . \quad (3)$$

When this expression is integrated for the conditions $N=N_m$ when $t=\infty$; and $N=0$ when $t=0$, then, the quantity, N, of niton present in the system at the time will be

$$N=N_m(1-e^{-\lambda t}) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where N_m represents the maximum or equilibrium value, and λ is the decay constant 0·180 when t is expressed in days. All the time the niton and the active deposit are being formed by the radium, the occluded niton is decaying according to the law previously described. Hence, the quantity of niton reaches half-value in about 3·85 days; 75 per cent. in 7·70 days; 99·55 per cent. in 30 days; and in 50 days. 99·99 per cent. of the equilibrium value is present. The rate of production of niton is $1{\cdot}24\times10^{-9}$ c.c. per sec. per gram of radium. In 1910, the Radiology Congress at Brussels [7] decided to call the amount of emanation or niton in equilibrium with a gram of pure radium a **curie**; smaller units are designated in the usual manner, thus the *millicuries* means the amount of emanation in equilibrium with

10 mgrms. of pure radium. A. Piccard and E. Stahel, and T. Nogier have raised the question of the constancy of the radioactivity of the standard tubes. E. A. Owen and B. Naylor discussed the measurement of the radium content of sealed tubes.

Since each α-particle emitted by radium becomes an atom of niton, and about $3{\cdot}4\times10^{10}$ α-particles are emitted per sec. per gram of radium, then the number, q, of atoms of niton formed per gram per sec. is $3{\cdot}4\times10^{10}$. For equilibrium, dN/dt of (3) is zero, and hence, the number, N, of atoms of niton present per gram is $N=q/\lambda$; but $\lambda=2{\cdot}085\times10^{-6}$ per sec., hence, $N=1{\cdot}63\times10^{16}$. Under standard conditions one c.c. of gas contains $2{\cdot}78\times10^{19}$ mols., so that a curie of niton, supposed monatomic, occupies 0·59 c.mm. E. Rutherford obtained about 0·6 c.mm.; J. Danysz and W. Duane, 0·59 c.mm.; A. Debierne, 0·58 c.mm.; and R. W. Gray and W. Ramsay, 0·60 c.mm. Less accurate values were obtained by W. Ramsay and F. Soddy, and A. T. Cameron and W. Ramsay. For the action of radium emanation or niton on water, salt soln., gases, and organic products, see radium rays.

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§ 8. The Products of the Rapid Decay of Radium Emanation—Radium-A to Radium-C

The radium from which the emanation has been abstracted loses about 75 per cent. of its radioactivity, and it then emits practically nothing but the α-rays; the β- and the γ-ray activities are almost completely lost. The radioactivity of radium gradually returns to its original value on standing. Hence, it is inferred that radium is constantly generating and storing the emanation, and that the emanation is constantly decaying. The rate at which the radium then regains its activity is equal to the rate at which the emanation loses its radioactivity. The **radioactivity of normal radium is an equilibium value because the rates of production and disintegration of the emanation are evenly balanced.** While the dynamics of the transformation changes in radioactive matter seem to

follow similar laws to those which obtain in molecular changes with irreversible reactions. there is a marked difference in their behaviour towards changes of temp. and press. E. Rutherford[1] showed that the constants of the radioactive transformation are not affected by concentration, or the decomposition products. The effects of variations of *temperature* ranging from −186° to +2500° have been studied by W. Makower and S. Russ, H. W. Schmidt and P. Cermak, R. W. Forsyth, M. S. Curie and H. K. Onnes, W. Engler, etc. P. Curie and J. Danne observed the decay curves of the active deposits are influenced by changes of temp., but the work of H. L. Bronson, and A. S. Russell has shown that these results are due to differences in the volatilization or sublimation of the products when heated. E. Rutherford and J. E. Petavel noted that the high *pressure* developed in a bomb during the explosion of cordite—temp. 2500°, press. 1000 atm.—made no difference. A. Schuster, and A. S. Eve and F. D. Adams also showed that a press. of 2000 atm. had no appreciable influence. F. G. Donnan inferred that the energy given out on highly ex-energic changes must be greater in strong than in weak *gravitational fields*. To test this, E. Rutherford and A. H. Compton subjected radioactive material to a centri fugal acceleration over 20,000 times that of gravity, and found no perceptible change over 1 part in 1000, the limit of the method of measurement. H. H. Poole showed that the corpuscular radiations have no effect on the changes; W. P. Jorissen and J. A. Vollgraff found that *cathode rays* have no result; P. Weiss and A. Piccard showed that an intense *magnetic field* has no effect; and W. Marckwald, and L. Bruner and E. Bekier observed no change in the presence of an *electric discharge*. H. S. Shelton has emphasized the fact that the indifference of radioactive changes to temp. and other physical conditions must be a relative phenomenon, and a consequence of the limited range of our resources. The highest temp. of our laboratories—3000°—are feeble when contrasted with those ten times hotter, which prevail in the colossal furnaces revealed by stellar spectra of the hotter stars. Consequently, the indifference of radioactive changes to external conditions cannot be accepted as absolute. Suppose, he adds, that electricity were unknown and it was only possible to attain variations of temp. of a few degrees in our laboratories, then a large number of so-called compounds would be classed as elements, and the slow decomposition of many substances with the evolution of heat would appear as marvellous sources of energy, as unaccountable as radioactive changes are to-day.

The processes of decay and restoration cannot be influenced by any known controllable physical or chemical force; they are independent of the chemical form of radium—chloride, bromide, carbonate, sulphate, metal, etc.—all that can be done is to study the mode and measure the rate of change. Hence, rightly or wrongly, it has been inferred that the process is a property of the radium *atom* alone; that the radium atoms break down into atoms of the emanation; and the atoms of the emanation break down into a radioactive solid, the so-called **active deposit,** and helium gas. This recalls the step-by-step decomposition of potassium hypochlorite into potassium chlorate, perchlorate, and chloride as well as oxygen. By analogy with the evolution of heat which attends certain exothermal chemical reactions—*e.g.* the decomposition of ozone, $2O_3 \rightarrow 3O_2 + 68{\cdot}2$ Cals.—it has been stated as an hypothesis that the origin of the energy of radioactive bodies is due to the decomposition of the atoms—a reaction accompanied by the liberation of charged particles. In the one case, the atoms re-form new and more stable combinations, and in the other case, the liberated particles are de-electrified and form helium. According to this hypothesis, a radioactive substance must have a more or less limited period of existence of life.

Radium emanation quickly breaks down into a new substance called radium-A, which has a half-life period of about 3 minutes, and passes into radium-B; and this, in turn, to radium-C; radium-C to radium-D; radium-D to radium-E; and radium-E to radium-F. Since the radioactivity due to radium-D, -E, and -F is negligibly small in comparison with that due to radium-A, -B, and -C—the initial radioactivity of the former being usually less than 10^{-5} of that of the latter—

E. Rutherford [2] found it convenient to analyze the active deposit of radium produced by the condensation and decay of radium emanation into (i) the **deposit of rapid change** (radium-A, -B, and -C); and (ii) the **deposit of slow change** (radium-D, -E, and -F). Hence, radium normally contains all three products—radium proper, the emanating gas, and the active deposit. It is estimated that 25 per cent. of the radiations of normal radium belong to radium proper; 18 per cent. more of the α-rays belong to the emanating gas; and the remaining 57 per cent. to the active deposit. W. Mund studied the effect of an electric field on the distribution of the active deposit of radium. The rate of rise of γ-ray activity from radium emanation has been measured by F. P. Slater.

As previously indicated, the active deposit of radium was discovered by M. S. and P. Curie; and measurements of its radioactivity were made by E. Rutherford and H. T. Brooks, and P. Curie and J. Danne. The latter found that the radioactivity I of the active deposit at the time t secs. (disregarding the first 20 mins. so as to ensure the death of radium-A) could be represented by $I=I_0(4{\cdot}20e^{-0{\cdot}000413t}-3{\cdot}20e^{-0{\cdot}000538t})$, where I_0 represented the initial radioactivity. E. Rutherford studied the decay of the activity of the deposit and found that the results could be explained on the assumption that three consecutive changes are involved, in which radium emanation passes directly to **radium-A,** the latter to **radium-B,** and that to **radium-C$_1$** and **radium-C$_2$.**

*Assuming that radium-*A *passes through a series of consecutive changes forming radium-*B, *radium-*C, . . . *it is required to find the concentrations of* -A, -B, -C . . . *respectively, at the end of a period of time t.* If P atoms of a substance A change into another B during the time t, it has been shown, (1) and (2), that $dP/dt=-P$, or $P=P_0e^{-\lambda_1 t}$, where λ_1 is the radioactive constant for the change A$\rightarrow$B, and P_0 is the number of atoms of A originally present. Let dQ represent the increase in the number of atoms of B in unit time; then dQ is the number supplied by the change of the matter A less the number due to the change of the substance B into C, or

$$\frac{dQ}{dt}=\lambda_1 P-\lambda_2 Q \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where λ_2 is the radioactive constant for the change B$\rightarrow$C. Substituting $P=P_0e^{-\lambda_1 t}$, and integrating

$$Q=P_0\frac{\lambda_1}{\lambda_2-\lambda_1}(e^{-\lambda_1 t}-e^{-\lambda_2 t}). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Similarly, when A changes to B, and B to C, if R represents the number of particles of C formed in the time t,

$$\frac{dR}{dt}=\lambda_2 Q-\lambda_3 R \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where λ_3 is the radioactive constant for the change C$\rightarrow$D. Substituting for Q, and integrating,

$$R=P_0(k_1e^{-\lambda_1 t}+k_2e^{-\lambda_2 t}+k_3e^{-\lambda_3 t}) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$k_1=\frac{\lambda_1\lambda_2}{(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)} \qquad k_2=\frac{\lambda_1\lambda_2}{(\lambda_3-\lambda_2)(\lambda_1-\lambda_2)} \qquad k_3=\frac{\lambda_1\lambda_2}{(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)}$$

and so on for n products. For radium-A, radium-B, and radium-C, $\lambda_1=0{\cdot}2273$, $\lambda_2=0{\cdot}02585$, and $\lambda_3=0{\cdot}03554$ per min., so that $k_1=1{\cdot}1520$, $k_2=3{\cdot}0102$, $k_3=-3{\cdot}1622$. Starting with one unit of radium-A, and none of radium-B or radium-C, the relative amounts of A, B, and C, obtained by calculation from equations (5) to (8), after the lapse of a specified time (minutes), are:

Time . .	1	5	10	16	40	100	200	400
A . .	0·7967	0·3210	0·1033	0·0261	0·0001	—	—	—
B . .	0·2009	0·6313	**0·7558**	0·7176	0·4019	0·0851	0·0064	0·00003
C . .	0·0029	0·0486	0·1238	0·2037	**0·3079**	0·1364	0·0145	0·00007

The corresponding curves are illustrated by Fig. 13. The numbers in clarendon type represent maxima in the curves. A. Piccard has discussed the drawing of the decay curves of radioactive substances. These and other relations have been discussed by E. Rutherford, and H. Bateman. They resemble analogous problems in the theory of ordinary consecutive reactions. Suitable modifications can be introduced when A, the primary source, is suddenly exhausted. H. Levy has suggested a criterion for finding the number, n, of radioactive transformations from a set of observations.

Values for the at. wt., the radioactive constants, the half-life period, and the average-life period of radium-A, -B, -C_1, and -C_2, were calculated by E. Rutherford, P. Curie and J. Danne, M. S. Curie, and H. L. Bronson :

	Emanation.	Radium-A.	Radium-B.	Radium-C.
Radioactive constant . .	$2{\cdot}085\times10^{-6}$	$3{\cdot}85\times10^{-3}$	$4{\cdot}33\times10^{-4}$	$5{\cdot}928\times10^{-4}$
	$1{\cdot}25\times10^{-4}$	0·231	0·0258	0·0355
Half-life period . . .	$55{\cdot}44\times10^{4}$	3	26·8	19·5
Average-life period . . .	$79{\cdot}92\times10^{4}$	4·32	38·7	28·1
Atomic weight . . .	222	218	214	214

Radium-A has such a short life that it can be but imperfectly isolated, observations must be made on it immediately after its production from niton. P. Curie and J. Danne found that the decay curves of the active deposit were much influenced by heating it to a high temp., and H. L. Bronson showed that these effects are not due to the effect of temp. on the rate of transformation of the radioactive products; but were produced by the different volatilities of the three products. He found radium-A volatilized more readily than radium-B; and radium-B, more readily than radium-C. According to F. Soddy, if a negatively charged wire is exposed for a few seconds only in a relatively large quantity of radium emanation, the activity of the wire at first is almost entirely due to the α-rays of radium-A, and these decay to a very small value in a few minutes after withdrawal of the wire from the emanation, the activity of the subsequent products formed being, for such short exposures, usually negligible. After twenty to thirty minutes' exposure to the emanation, the quantity of radium-A attains equilibrium and does not further increase. But the amounts of radium-B and -C on the wire go on increasing with the time of exposure up to three or four hours. Obviously the shorter the time of exposure the purer is the radium-A deposited. Conversely with a wire which has been exposed any length of time to the emanation, no radium-A remains after twenty to thirty minutes from withdrawal, the activity at this stage being due to radium-B. Hence, without chemical treatment, radium-A alone or radium-B and -C, together, may be obtained at will by a suitable choice of the time of exposure to the emanation, and of the time elapsing after withdrawal from its influence.

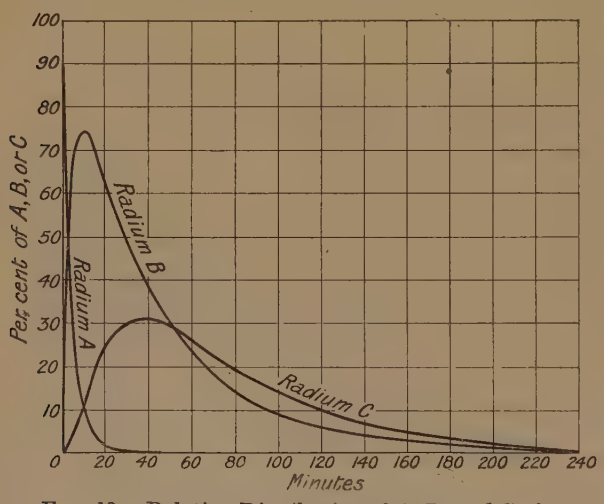

FIG. 13.—Relative Distribution of A, B, and C after different Intervals of Time.

If a negatively charged wire be kept in niton for a long time, the amount of radium-A which accumulates on the wire soon assumes the stationary state when the rate of production is equal to the rate of decay; the amounts of radium-B and radium-C continue increasing for many hours. F. von Lerch [3] has reviewed the methods available for separating the radium-A, -B, and -C decay products.

W. Makower heated a wire to 900° in radium emanation, but was unable to collect radium-A, -B, and -C, whether the wire was charged negatively or positively. P. Curie and W. Duane stated that at 600°, radium-B could be volatilized freely from a plate coated with the active deposit, while radium C- remained behind.

The volatilization of radium-C was found by W. Makower to depend upon the surface on which it was deposited ; thus, the volatilization of radium-C is appreciable at all temp., and all the radium-C passed off from platinum and nickel at 1200°, but from quartz, the volatilization was incomplete at 1300°. A. S. Russell, and H. Schrader have studied the nature of the surrounding gases on the volatilization. It is quite possible that oxides or other compounds may be formed. Many volatilized products deposit at a much lower temp. in ozone than in oxygen. The temp. required for the volatilization of radium-C in hydrogen is about 430°, and in oxygen about 1000° ; while radium-A is volatile in hydrogen at about 400°, and in oxygen at about 550°. According to H. L. Bronson, W. Duane, W. Makower, and A. S. Russell, radium-A volatilizes at about 900°, radium-B between 600° and 800°, and radium-C at 1100°. Hence it is possible to separate radium-B and radium-C by fractional volatilization.

O. Hahn and L. Meitner dissolved the active deposit in boiling hydrochloric acid, and allowed it to stand for three-quarters of an hour in order to allow all the radium-A to decay. When the acid liquid was agitated with animal charcoal, the radium-C is retained. The filtrate was treated with a barium salt and sulphuric acid, and the precipitated barium sulphate retained the radium-B. According to F. von Lerch, if cupric sulphate be added to the acid liquid, and a minute later, potassium hydroxide, radium-C was retained by the precipitate and radium-C remains in the filtrate. If lead nitrate be mixed with the hot acid liquid, and sulphuric acid added, radium-B is retained by the precipitate, and radium-C by the filtrate. If the acid liquid be electrolyzed with platinum electrodes, radium-C deposits on the cathode, while radium-B remains in soln. This shows that radium-C is rarer, *i.e.* less electropositive, than radium-B. F. von Lerch found that if a nickel or copper plate be dipped in the acid liquid, radium-C is precipitated while radium-B remains in soln. According to L. Meitner, the reaction is quantitative if a conc. boiling soln. be employed. T. Godlewsky found that in a neutral or feebly acid soln. of radium-B and radium-C, the latter, like bismuth, will be present in the colloidal form, possibly as a basic salt, the radium-B will be found in the filtrate. It will be observed that as soon as radium-B has been isolated it immediately begins to produce a fresh amount of radium-C by its own decay.

O. Hahn and L. Meitner, and W. Makower and S. Russ found that radium-B could be obtained in a pure state by recoil from radium-A, and that radium-C could be obtained from radium-B. The general method was to place an inactive plate charged negatively near a plate covered with active matter. The **recoil atoms** are concentrated on the negative plate in virtue of their positive charge. While the total amount of radium-C liberated by recoil is only about 1 in 6000, a considerable part of radium-A can be obtained by the recoil process. The collection of the recoil products on negatively charged plates proceeds most favourably in vacuo. It was once thought that radium-B is volatile at ordinary temp., but the apparent volatilization occurs only at the moment radium-B is being produced from radium-A ; when all the latter has disappeared, there is no sign of the volatilization of radium below a red heat. The apparent volatilization at ordinary temp. is really a recoil effect due to the projection of radium-B from the active deposit by recoil at the moment the α-particle is expelled from the atom of radium-A. The distribution and range of recoil atoms was studied by K. T. Compton, etc.

B. H. Herszfinkiel and L. Wertenstein [4] measured the heat transformation of radium-B to radium-C. E. Rutherford showed that radium-A emitted only α-rays and radium-C, α-, β-, and γ-rays ; while radium-B was at first thought to be rayless, but H. W. Schmidt found that radium-B emitted β-rays. These results were confirmed by K. Fajans and W. Makower, and F. von Lerch. H. G. J. Moseley and W. Makower showed that radium-B gives off as well readily absorbed γ-rays. The range and velocity of the α-particles of radium emanation are respectively 4·16 cms. and $1{\cdot}69 \times 10^9$ cms. per sec. ; the range of the α-particles of radium-A is 4·75 cms. ; and the range and velocity of the α-particles of radium-C are 6·94 cms.,

and $1{\cdot}92\times10^9$ cms. per sec. T. S. Taylor found the range of the α-particles of radium-C to be 6·93 cms. in air; 6·25 cms. in oxygen; 30·93 cms. in hydrogen; and 32·54 cms. in helium. The charge on the recoil atoms of radium-A and -B behaves similarly to that of the recoil atoms of niton, *q.v.* The decay curves of the α-rays of the active deposit were studied by H. L. Bronson. The curves of the β-rays were investigated by H. W. Schmidt, and H. L. Bronson, while K. Fajans and W. Makower showed that the β-rays from radium-B furnish two groups whose coeff. of absorption in aluminium are 91 cms. and 18 cms. The decay curves of the γ-rays were studied by H. G. J. Moseley and W. Makower. The recovery and decay curves were studied by E. Rutherford and J. Chadwick. According to H. W. Schmidt, the absorption coeff. of the β-rays of radium-B, in aluminium, are respectively 890, 80, and 13·1 cms.; E. Rutherford and H. Richardson gave for the absorption coeff. of the γ-rays of radium-B, in aluminium, 230, 40, and 0·51 cms. H. W. Schmidt gave for the absorption coeff. of the β-rays of radium-C in aluminium 1·3 and 53 cms.; and for the γ-rays, 0·115 cm. of aluminium, or 0·5 cm. of lead. H. Richardson also found a salt γ-radiation with an absorption coeff. of 40 cms. in aluminium. According to E. Rutherford and H. Robinson, and J. Chadwick, the magnetic spectra of the β-rays of radium-B and radium-C are very complex. H. G. J. Moseley and H. Robinson found that the β-rays of radium-B in equilibrium with a gram of radium, furnish $0{\cdot}325\times10^{15}$ pairs of ions corresponding with an energy of 1·71 cals. per hour; the γ-rays similarly give $0{\cdot}084\times10^{15}$ pairs of ions corresponding with 0·44 cal. per hour; the β-rays of radium-C likewise gave $0{\cdot}64\times10^{15}$ pairs of ions corresponding with 3·35 cals. per hour; and the γ-rays, $1{\cdot}134\times10^{15}$ pairs of ions or 5·96 cals. per hour. J. Szmidt found the distribution of energy in radium-B and radium-C in equilibrium with one another for the soft rays of radium-B; the hard rays of radium-B; rays from radium-C=1 : 45 : 639; or $0{\cdot}01\times10^4$, $0{\cdot}49\times10^4$, and $6{\cdot}92\times10^4$ ergs per sec. C. D. Ellis studied the magnetic spectrum of the β-rays of radium-B.

It is generally assumed that radium-A is isotopic with polonium, and closely related with tellurium; that radium-B is isotopic with lead; and radium-C with bismuth. According to J. Patkowsky,[5] the radium atom derived from radium emanation deposits on different metals in approximately the order of the electrochemical series; thus, 14 per cent. more deposits on silver than on aluminium. According to E. Ramstedt, radium-B and -C deposited on glass surfaces from the emanation give more regular solubility results than when deposited on gold or platinum. Only about one-half (mean 0·52) of the active deposit on a glass surface is readily dissolved; the other half is not dissolved at all on boiling with acid, but with gold and platinum the soluble part amounts to 60–70 per cent. This is explained by the recoil of the radium-B particle in its formation from radium-A, driving it into the surface. For radium-B deposited on a plate by projection from a radium-A surface the whole is soluble. Radium-C is soluble in the common acids, less so in alkaline liquids and in water, and very little in organic solvents. Radium-B dissolves more quickly than radium-C in water and acids, especially when dil., less quickly in alkaline liquids and very little in organic solvents. Radium-A is more soluble than radium-B and -C, and dissolves even in organic solvents, especially carbon disulphide, which confirms its position in the sulphur family of elements. The speed of soln. increases with the temp. of the solvent, and S. Arrhenius's formula applies approximately. It was found by depositing the active material on plates of gold and platinum previously saturated electrolytically with hydrogen and ogygen that oxygen enormously diminishes the solubility, especially of radium-C, whilst hydrogen diminishes the relative speed of soln. of radium-A. The influence of oxygen on solubility is analogous to that on volatility. A. Fleck discussed the isotopy of radium-B and actinium-B, and of radium-C, thorium-C, actinium-C, and bismuth.

Radium-C emits α-, β-, and γ-rays, and since most substances emit either α-rays or β- and γ-rays, O. Hahn and L. Meitner [6] tested by the recoil method the nature of radium-C deposited on nickel from an acid soln. of the active deposit. They

obtained evidence showing that radium-C is a complex product which deposits a short-lived substance **radium-C_2** on a negatively charged plate. K. Fajans found radium-C_2 separated by recoil, emitted β-rays but no γ-rays. The β-rays had approximately the same penetrating power as those emitted by radium-C. The amount of radium-C_2 obtained by recoil was small and possessed only about $\frac{1}{6000}$th of the β-ray activity of the parent radium-C. Radium-C produced radium-D by recoil in approximately the amount required for a vigorous α-ray recoil. The small amount of radium-C_2 so obtained indicated that it could not be a direct product of radium-C. K. Fajans and W. Makower further showed that radium-C_2 could not be in the main line of descent from radium-C_1, but must be a side product. Hence radium-C_1 breaks up in two ways; about 99·97 furnishes radium-D, with the emission of β- and γ-rays, and a small fraction, about 0·03 per cent., with the emission of α-rays, furnishes radium-C_2. The decay products from the emanation are therefore:

$$\text{Nt}\rightarrow\text{RaA}\rightarrow\text{RaB}\rightarrow\text{radium-C}\begin{cases}\rightarrow\text{radium-C}_2\rightarrow\ ?\\ \rightarrow\text{radium-D}\rightarrow\text{radium-E}\rightarrow\end{cases}$$

The transformations along the side chain radium-C_2 have not been closely followed. The at. wt. of radium-C_2 is probably 210; the half-life period, 1·38 mins.; the average life period, 1·99 mins.; the radioactive constant $\lambda=0{\cdot}495$ min. or $8{\cdot}4\times10^{-3}$ secs.; the absorption coeff. for the β-rays is 13 and 53 cms. of aluminium. In its decay, radium-C_1 gives α-rays, radium C_2 gives off β- and γ-rays; the initial velocity of the β-rays is $2{\cdot}4\times10^{10}$ to $2{\cdot}94\times10^{10}$ cms. per sec. E. Albrecht obtained for the velocity-ratio Ra-C_2 : Ra-C$=0{\cdot}0004$. C. D. Ellis, and J. Neukirchen measured the wave-lengths of the γ-rays from radium-C.

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§ 9. The Products of the Slow Decay of Radium Emanation—Radium-D to Radium-F

M. S. Curie,[1] F. Giesel, and E. Rutherford found that the activity of the deposit obtained by exposing a body to radium emanation does not all disappear when removed from the emanation ; rather does a small residual activity remain, the magnitude depending on the quantity of the emanation, and the time of exposure. The α-ray activity of the matter remaining after the decay of the products of the rapid transformation gradually increases with time and after 300 days the curve approaches a maximum value ; and the β-ray activity approaches a maximum in about 40 days. The phenomena are interpreted to mean that the residual active matter consists of the products of three successive changes—radium-D, radium-E, and radium-F. Radium-D gives off slow β-rays, and very soft γ-rays ; radium-E both β-rays and weak γ-rays ; and radium-F gives off α-rays. K. Fajans showed that radium-D is derived directly from the decay of radium-C ; the former can be obtained by recoil from the latter.

J. Elster and H. Geitel observed that the lead separated from pitchblende was markedly reactive, owing, it was said, to the presence of small quantities of radium and polonium ; K. A. Hofmann and E. Strauss, however, concluded that the lead separated from uranium minerals contained a new radioactive substance which they called *radio-lead*—a similar term, *radium lead*, was later applied to radium-G. The preparation of radio-lead from uranium minerals (not autunite) described by K. A. Hofmann and co-workers is as follows :

The chloride or nitrate soln. is stirred with 0·02 eq. of sulphurous or sulphuric acid ; after standing 14 days, the mixture is filtered, and the precipitate washed. The radio-lead is also separated from polonium by the fractional crystallization of the nitrate ; or by decomposition with sodium thiosulphate ; or by the electrolysis of the nitrate in warm dil. nitric acid. In another process, the chloride is digested for 10 hrs. at 35°, with an equal weight of fuming hydrochloric acid free from sulphuric acid ; the soln. evaporated to $\frac{1}{20}$th of its volume ; made up to one-fourth of its original volume with hot water.

The filtrate containing about half per cent. of free hydrochloric acid, is treated with hydrogen sulphide, and the sulphide washed with dil. hydrochloric acid and then with ammonium sulphide.

K. A. Hofmann's radio-lead was shown by E. Rutherford to contain radium-D, radium-E, and radium-F ; and, when freshly prepared, **radium-D,** as the primary radioactive constituent. Radium-D is almost rayless, and when purified, as first described, radio-lead appears inactive ; but radioactivity is generated in the course of time owing to the partial decay of radium-D into radium-E and radium-F. The chemical and physical properties of radium-D and lead are so similar that, in spite of the attempts of K. A. Hofmann and V. Wölfl, F. Paneth and G. von Hevesy, B. Szilard, and H. Herschfinkel no satisfactory method has been found for concentrating the radioactive constituent, radium-D, from the lead.

Among the unsuccessful methods tried are (i) by precipitation of chloride soln. at 100° with dil. sodium thiosulphate and with hydrochloric acid ; (ii) by precipitation with quadrivalent lead compounds, by precipitation of a lead chloride soln., sat. with chlorine, with ammonium chloride, whereby plumbichloride is precipitated ; by passing sulphur

dioxide through a soln. sat. with lead chloride and hydrogen chloride, whereby the lead chloride is fractionally precipitated; and by precipitation of lead dioxide by addition of hydrogen dioxide or bromine water to a soln. of lead hydroxide in sodium hydroxide, or of bromine water to lead acetate; (iii) by adsorption methods, as by precipitation of barium sulphate or silicofluoride in lead nitrate soln., or barium chloride in a lead chloride soln. by saturating with hydrogen chloride; also by separating iron from lead chloride soln. by the acetate precipitation, by adding potassium permanganate and alcohol to lead chloride soln., and by boiling the latter with flowers of sulphur; (iv) by distillation of lead chloride in carbon dioxide at 1000°; (v) by electrolysis in soln., under varying conditions, so that part of the lead separates on the cathode and part on the anode as dioxide, and of molten lead chloride, pure or mixed with potassium chloride; (vi) by dialysis of lead nitrate through parchment paper or animal membrane and diffusion of lead chloride soln.

It is therefore inferred that the radium-D and lead are isotopic. According to F. Soddy, common commercial lead contains traces of radium-D which makes lead more radioactive than most of the other metals. If lead is desired free from radioactive products, old lead should be used, since the active constituents will presumably have decayed.

A. T. Cameron and W. Ramsay found that after a large quantity of purified emanation had been allowed to decay in a small capillary, a black, sub-metallic film appeared, and this was ascribed to the decay of the emanation into radium-D. This is the simplest method of purifying radium-D free from elements other than those belonging to the radium series. Another source of radium-D is in old radium preparations kept in a solid state, or under such conditions that the emanation is retained; radium-D steadily accumulates in the system until about 8 mgrms. of radium-D are present per gram of radium; and it can be separated from radium-E, and radium-F, by precipitation with sulphuric acid; the radium-D is separated from radium by adding a little lead and separating the lead by hydrogen sulphide—radium-D follows the lead.

The at. wt. of radium-D is about 210. G. von Hevesy and F. Paneth found the diffusion constant of radium-D is characteristic of that of a bivalent element being 0·65 sq. cm. per day. E. Rutherford found radium-D is volatile at a high temp. The rays emitted by radium-D are so feeble in comparison with those of radium-E, that E. Rutherford at first thought radium-D is rayless; O. von Bäyer, O. Hahn, and L. Meitner, however, detected feeble β-rays with an initial velocity of $2{\cdot}31\times10^{10}$ cms. per sec.; the β-rays consists of two homogeneous beams emitted with 0·31 and 0·37 of the velocity of light, or with velocities $0{\cdot}99\times10^{10}$ cms. per sec. A. F. Kovarik showed that the absorption coeff. of the β-rays in aluminium is 130 cms.$^{-1}$. L. Meitner thinks this too large and gives 5500 cms.$^{-1}$. Radium-D thus furnishes the softest known γ-rays. L. Meitner studied the γ-rays from radium-D. E. Rutherford and H. Richardson found evidence of feeble γ-rays with absorption coeff. in aluminium of 45 and 0·99 cms.$^{-1}$. The transformation of radium-D into radium-E is too slow to permit direct observations except over a period of years. E. Rutherford estimated its half-life period to be 40 yrs.; and S. Meyer and E. von Schweidler 37·5 yrs. Later determination by E. Rutherford, R. Thaller, M. S. Curie, and G. N. Antonoff gave for the half-life period, 16·5 yrs.; for the average-life period, 23·8 yrs.; and for the radioactive constant $\lambda=0{\cdot}0433$ yr., $1{\cdot}18\times10^{-4}$ days; $4{\cdot}94\times10^{-6}$ hrs.; $8{\cdot}22\times10^{-8}$ mins.; or $1{\cdot}37\times10^{-9}$ secs. R. W. Lawson found that if polonium is deposited by electrolysis on a clean metal foil it is found subsequently that, at normal press. and in vacuo, surrounding objects become active also. The phenomenon can be explained on the supposition that aggregates of polonium atoms are carried off from the active surface and deposited on neighbouring surfaces.

The spectrum of radium-D has not been satisfactorily determined. E. Demarçay attributed the lines 3659·6 and 4116·8 in the spectrum of radio-lead to radium-D, but the former possibly belongs to molybdenum, and the latter to vanadium G. von Hevesy and F. Paneth inquired whether the inseparability of lead and radium-D is due to our ignorance of a suitable method, or to the identity of the properties of the two elements. It was inferred that two elements are chemically

identical, *i.e.* isotopic, when they are electrochemically replaceable. They found that cells of radium-D dioxide and nitrate and of lead dioxide and nitrate gave the same difference of potential, and that ions added to both cells gave the same change of potential.

The growth of the β-ray activity of radium-D, and the subsequent appearance of α-rays, shows that radium-D probably decays into **radium-E.** When a mixture of radium-D, radium-E, and radium-F is heated to over 1000°, E. Rutherford found that the greater part of the first and the last are volatilized while radium-E remains. The *β-strahlende Bestandteil* of K. A. Hofmann's *radio-lead*, is identical with radium-E. S. Meyer and E. von Schweidler thought that radium-E is a complex of radium-E and radium-E_2, because it furnished two β-ray products with half-life periods of 4·8 and 6·2 days. It was said that at a red heat radium-E_1 is volatile, and that radium-E_2 is not volatile; and that when an electro-deposited film is treated with hot acetic acid, radium-E_1 dissolves while radium-E_2 remains insoluble. G. N. Antonoff, however, showed that there is only one β-ray product with a half-life period of about 5 days. F. Giesel separated a β-ray product with a half-life period of 6 days from polonium, and he called it *β-polonium*—this is taken to have been radium-E. In its chemical behaviour, radium-E behaves like bismuth with which it is isotopic.

According to S. Meyer and E. von Schweidler, if a soln. of lead chloride containing radium-D, radium-E, and radium-F be boiled with nickel, palladium, iridium, or silver foil, radium-E is alone deposited on the metal. If much lead chloride be present, it is advisable to first crystallize out the lead salt. In old radium preparations containing radium-D, radium-E, and radium-F, the first named can be precipitated with the radium sulphates; radium-E and radium-F remain in soln. When a soln. of a lead salt, containing radium-E and radium-F, is electrolyzed with about 4 microamps., *i.e.* 4×10^{-6} amps. per sq. cm., radium-F is first deposited on the cathode, and on increasing the current density to 10 microamps. per sq. cm., a mixture of radium-E and radium-F is precipitated; and with a current of 10^{-4} amp. lead (and radium-D, if present) is deposited. This is in accord with *F. von Lerch's rule:* the successive products of a disintegration series is accompanied by a regular increase in the electro-negative character, the successive products being each electrochemically nobler than the last, and therefore more easily deposited in electrolysis. As a rule, the successive products of the disintegration series become more volatile, and more soluble in acids.

G. von Hevesy and F. Paneth found that the diffusion coeff., 0·45 sq. cm. per day, agrees with the assumption that radium-E is tervalent, and belongs to the bismuth family. According to S. Meyer and E. von Schweidler, and E. Rutherford and H. Richardson, radium-E gives off β rays which have an absorption coeff. in aluminium of 43 cms.$^{-1}$; the magnetic spectrum gave no sharp separations; the average velocity of the β-rays is $2\cdot3\times10^{10}$ cms. per sec. The γ-radiations are extraordinarily feeble, being less than 0·3 per thousandth of the β-radiations, and have an absorption coeff. resembling that of radium-D. J. A. Gray found that the primary γ-rays of radium-E are able to excite characteristic radiations in elements of at. wt. between silver and didymium. The half-life period has been estimated by E. Rutherford, F. Giesel, J. Danysz, G. N. Antonoff, M. S. Curie, and L. Meitner; the best representative value is 5 days; while the average-life period is 7·2 days. The radioactive constant is $\lambda=1\cdot66\times10^{-6}$ secs., $9\cdot96\times10^{-5}$ mins., $5\cdot95\times10^{-3}$ hrs., 0·1429 day, 52·19 yrs.

The first radioactive substance separated in 1898 by M. S. Curie from uranium minerals was named **polonium** after the native country of M. S. Curie. It appeared with bismuth in the precipitate obtained with hydrogen sulphide during the isolation of radium (*q.v.*). W. Marckwald obtained a radioactive precipitate by immersing a polished bismuth plate in a soln. prepared from uranium minerals; the precipitate also contained tellurium and the radioactive constituent was consequently called *radio-tellurium;* S. Meyer and E. von Schweidler also called it *radioactive bismuth.*

These products as well as the *α-ray product in radio-lead* and the α-ray stage in the decay of radium-E are all thought to be identical; their half-life periods are the same within the limits of experimental error. When it is desired to emphasize the fact that polonium is a decay product of radium-E, it is called **radium-F.** A. Fleck discussed the origin of radium-F.

M. S. Curie showed that the radioactivity of the sulphides precipitated from acid soln. of pitchblende by hydrogen sulphide, is due to the presence of polonium. There are also present sulphides of bismuth, copper, lead, and a little antimony and arsenic. She employed the following process for isolating the active sulphide:

The soln. made strongly acid with hydrochloric acid are precipitated with hydrogen sulphide; the sulphides thus precipitated are very active, and are employed for the precipitation of polonium; there remain in the soln. substances not completely precipitated in presence of excess of hydrochloric acid (bismuth, lead, antimony). To complete the precipitation, the soln. is diluted with water, and treated again with hydrogen sulphide, which gives a second precipitate of sulphides, much less active than the first, and which have generally been rejected. For the further purification of the sulphides, they are washed with ammonium sulphide, which removes the last remaining traces of antimony and arsenic. They are then washed with water and ammonium nitrate, and treated with dil. nitric acid. Complete soln. never occurs; there is always an insoluble residue, more or less considerable, which can be treated afresh if it is judged expedient. The soln. is reduced to a small volume and precipitated either by ammonia or by excess of water. In both cases the lead and copper remain in soln.; in the second case, a little bismuth, scarcely active at all, remains also in soln.

The precipitate of oxides or basic nitrates is fractioned by dissolving the precipitate in nitric acid and adding water to the soln. until a sufficient quantity of precipitate is formed. It must be borne in mind that sometimes the precipitate does not at once appear. The precipitate is separated from the supernatant liquid, and re-dissolved in nitric acid, after which both the liquids thus obtained are re-precipitated with water, and treated as before. The different fractions are combined according to their activity, and conc. is carried out as far as possible. In this way is obtained a very small quantity of a substance of which the activity is very high, but which, nevertheless, has so far only shown bismuth lines in the spectroscope. There is, unfortunately, little chance of obtaining the isolation of polonium by this means. The method of fractionation just described presents many difficulties, and the case is similar with other wet processes of fractionation. Whatever be the method employed, compounds are readily formed which are absolutely insoluble in dil. or conc. acids. These compounds can be re-dissolved only by reducing them to the metallic state, *e.g.* by fusion with potassium cyanide. Considering the number of operations necessary, this circumstance constitutes an enormous difficulty in the progress of fractionation.

In addition to the conc. of the active sulphide by precipitation with hydrogen sulphide from a conc. soln. in hydrochloric acid—polonium sulphide is less soluble than those of bismuth or lead—and the precipitation of the basic nitrate with water, whereby polonium accumulates in the precipitate, M. S. Curie sublimed the mixed sulphides in vacuo, and found that polonium sulphide is more volatile than that of bismuth. W. Marckwald treated the hydrochloric acid soln. of radioactive bismuth chloride from pitchblende with metallic bismuth or antimony, and found the radioactive matter deposited as a black film. This film is nearly all tellurium since pitchblende contains about 0·01 per cent. of tellurium. To remove tellurium, the metal was dissolved in hydrochloric acid, and the tellurium precipitated by hydrazine hydrochloride; the operation was repeated a number of times. The filtrate containing bismuth, tin, selenium, and tellurium was conc. by evaporation, treated with a few drops of stannous chloride, and digested on the water-bath. The precipitate was again dissolved in nitric acid, evaporated with hydrochloric acid to drive off the nitric acid, and the soln. treated with sulphur dioxide. The precipitate was again dissolved in nitric acid, evaporated to dryness, and warmed with ammonia. The amount of residual radio-tellurium corresponded with 3 mgrms. per 15 tonnes of pitchblende. W. Marckwald also found that when plates of bismuth, copper, or silver are immersed in the hydrochloric soln., nearly all the polonium is deposited on the plates. M. S. Curie and A. Debierne also, instead of treating the hydrochloric acid soln. with hydrogen sulphide, introduced an iron plate and found copper, bismuth, lead, arsenic, antimony were precipitated. The precipitate was dissolved in hydrochloric acid, and treated with copper plate; this was again dissolved

in acid, and treated with stannous chloride as indicated above. H. M. Plum employed a similar process in the separation of polonium from carnotite. According to F. Paneth, the separation of radium-E and polonium from radio-lead by dialysis is due to the fact that radium-E and polonium are both easily hydrolyzed in aq. soln. The basic salts or hydroxides thus formed remain in soln. as colloids, and consequently do not pass through the membrane with lead and radium-D. If, on the other hand, a nitric acid soln. of radioactive lead is dialysed, there is no separation. G. von Hevesy found that the more basic radioactive products dissolve more rapidly in neutral, alkaline, or weakly acid soln. than the nobler ones.

The electrolytic separation of radium-D and radium-E in radio-lead by S. Meyer and E. von Schweidler's process has already been described. G. von Hevesy and F. Paneth studied the decomposition potential of polonium in $10^{-8}N$-soln., and N-soln. with respect to nitric acid and gold electrodes. Gold was employed because it has no special affinity for polonium, which is deposited, from vapour, preferentially on platinum and palladium. Nitric acid removes all but 0·5 per cent. of the polonium electrochemically deposited on gold, but leaves 13 per cent. in the case of platinum. Under similar conditions the ratio of the amounts of polonium deposited on gold and platinum electrodes are as 2 : 3. The polonium used was estimated to be in $10^{-8}N$-soln. By gradually increasing the current strength the cathode and anode potentials were gradually raised. A sudden increase was noted in the cathode at E_{Hg}=0·35 volt and on the anode at E_{Hg}=1·05 volts, Fig. 14. The anodic deposition is to be explained, as with manganese and lead, as being due to the deposition of a peroxide of polonium. Diffusion experiments show that polonium is bivalent, and the normal potential of polonium, calculated from the decomposition potential at $10^{-8}N$, is 0·35+8×0·028=0·57 volt. This lies near the normal potential of silver. The calculated normal potential of polonium peroxide, in $10^{-3}N$-nitric acid, is +0·89 volt, that of lead being 0·82 volt. By varying the conditions it is possible to confine the deposition of polonium to the anode or cathode at will, and the fractional deposition of polonium as peroxide can be used to separate it from metals, such as gold, mercury, etc., which are not anodically deposited. Owing to the tendency to form colloidal soln., neutral or weak acid soln. are to be avoided, $10^{-1}N$-nitric acid being suitable.

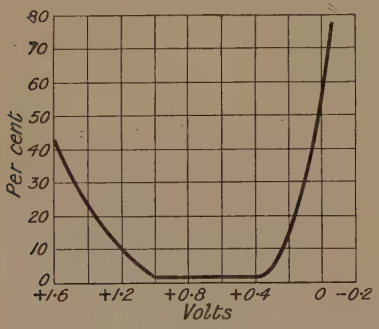

Fig. 14.—Decomposition Potential of Polonium.

F. Paneth and G. von Hevesy extracted polonium from the lead nitrate derived from pitchblende in the following manner. The yield was about 80 per cent. The hot sat. soln. of the lead nitrate is left to crystallize, the mother liquor is separated by centrifuging, and after being slightly diluted is electrolyzed with platinum electrodes and a feeble current, a few mg. of bismuth being added to diminish the separation of radium-E. The cathode potential must not exceed −0·8 volt, which corresponds, in the soln. described, with 0·16 milliamp. per sq. cm., but if freedom from radium-E is desired, a potential of −0·5 volt or 0·4 milliamp. per sq. cm. may be used. Stirring is advantageous both in electrolysis and also on deposition on copper, which is an equally good method. If polonium free from lead and radium-D, but not from radium-E, is required, so much conc. nitric acid is added that lead is no longer cathodically deposited. Under these conditions most of the polonium can still be separated at the cathode. By volatilization at 1000°, all but 0·1 per cent. of the polonium may be removed from the electrodes, which is difficult to do by boiling with acids. The polonium vapour condenses preferably on palladium and platinum, in special degree on the former, rather than on gold, copper, nickel, or the walls of a quartz tube.

Old preparations of radium furnish radium-F: (i) by S. Meyer and E. von Schweidler's electrolytic process; or (ii) by treating the acidified soln. with hydrogen sulphide; on filtration, an invisible deposit of polonium sulphide will be found on the filter paper; or (iii) by dipping a piece of platinum or bismuth foil in the soln. when the polonium deposits on the metal. Radium-F can also be obtained from radium emanation which has stood for some months in a glass vessel. The excess of emanation is removed; the film deposited on the glass walls is dissolved in sulphuric acid; and the polonium precipitated by introducing a piece of bismuth foil in the soln.

The at. wt. of polonium is about 210. A. Muszkat, and H. Herschfinkiel consider polonium and radium-A are isotopic. The chemical properties of polonium are closely related to those of bismuth, and still more closely to those of tellurium; but these elements are not isotopic. Polonium stands below tellurium in the vertical column of the periodic table when the elements are arranged according to their atomic numbers. The compounds are easily hydrolyzed, reduced, and electrolyzed. In analysis, polonium follows bismuth, from which it is separated as described above. F. Paneth, and R. W. Lawson prepared volatile *polonium hydride* by passing hydrogen over electro-deposited polonium heated to 700°–900° in a quartz tube; and F. Paneth, by allowing electro-deposited polonium to act on ionized hydrogen. Polonium can be alloyed with palladium and platinum; and, according to G. Costanzo, palladium occludes radium-A which is isotopic with polonium. According to F. Paneth, polonium and radium-E are colloidal in neutral soln., radium-D in ammoniacal soln. While radium does not assume the colloidal form in neutral or alkaline soln., polonium migrates towards the cathode in acid soln., and towards the anode in ammoniacal soln. G. von Hevesy and F. Paneth found the coeff. of diffusion, 0·76 sq. cm. per day, in feebly acid soln., is characteristic of a bivalent metal, but in alkaline soln., say $\frac{1}{2}N$-NH_3, the coeff. is 0·19 sq. cm. per day.

According to P. Curie, O. Wigger, B. Kucera and B. Masek, M. Levin, S. Meyer and co-workers, W. Michl, H. Gieger and J. M. Nuttall, E. Rutherford, and R. W. Lawson, radium-F emits α-particles with a range of 3·77 cms. in air at 15°, and with a velocity $1{\cdot}61\times10^9$ cms. per sec. T. S. Taylor found at 15° a range of 3·77 cms. in air, 3·43 cms. in oxygen, 16·83 cms. in hydrogen, and 17·52 cms. in helium. I. Curie found the velocity of the α-rays of polonium to be 1593×10^9 cms. per sec. A. Muszkat and L. Wertenstein studied the fluctuations of the α-radiations of polonium. M. S. Curie showed that the α-rays from polonium produce chemical and physical effects like those of radium. A milligram of polonium, however, emits as many α-particles as 5 grms. of radium. The α-rays are homogeneous, and no β-rays are emitted. The half-life period, determined by M. S. Curie, S. Meyer and E. von Schweidler, F. Giesel, H. Becquerel, E. Rutherford, W. Marckwald and H. Greinacher, J. W. Waters, E. Regener, and R. Girard, averages 136 days; and the average-life period, 196 days. The radioactive constant, $\lambda=5{\cdot}88\times10^{-8}$ secs.; $3{\cdot}528\times10^{-6}$ mins.; $2{\cdot}12\times10^{-4}$ hrs.; $5{\cdot}078\times10^{-3}$ days; or 1·855 yrs. M. S. Curie found that if θ denotes the mean interval between the emission of α-particles by polonium, the fraction of the total intervals of greater duration than τ, is $e^{-\theta/\tau}$. She found λ to be 0·00496 day^{-1}, corresponding with the average life 202 days, and the period of half-change 140 days. D. Bose found that about one in 1038 α-particles of polonium show a branching path in hydrogen gas. T. R. Wilkins studied the ionization produced by the α-rays from polonium. M. S. Curie and A. Debierne extracted from several tons of pitchblende 2 mgrms. of radioactive matter containing about 0·1 mgrm. of polonium. The spectrum showed the presence of many elements and of new lines 4642·0, 4170·5, 3193·6, and 3652·1, which were ascribed to polonium. Other lines were described but their connection with polonium is doubtful. The new lines are being periodically examined to find if they disappear and give place to the spectral lines of lead, suspected to be the product of the decay of radium-F. The saturation current produced between two infinitely extended plate electrodes by radium-F has been studied by G. Richter. Every α-particle from polonium

was observed by H. Geiger and A. Werner to produce a scintillation when it strikes a crystal of willemite. F. Paneth found evidence of the formation of a **polonium hydride** by the action of magnesium powder on soln. of salts of that element, and the compound was studied by F. Paneth and A. Johannsen.

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§ 10. The Progenitors of Radium

Uranium has a higher at. wt. than any other element; and it is also characterized by an unusually large number of spectral lines. F. Exner and E. Haschek,[1] for instance, record 4940 lines in the arc-spectrum, and 5655 lines in the spark-spectrum. These facts support the assumption that uranium is not a homogeneous element, and this view is in harmony with the evidence derived from a study of the radioactivity of this element. The early experiments of M. S. Curie had demonstrated that the radioactivity of uranium is an atomic property in that it is dependent only on the amount of that element present, and is not affected by the nature of other inactive elements with which it may be combined.

The genetic relationship between uranium and radium is emphasized by the fact that (i) Radium and uranium always occur together, and the two elements are not sufficiently common for this to be due to mere chance; and that, as previously shown, (ii) the proportion of radium to uranium in old uraniferous minerals is

almost invariable, being nearly 1 : 3,400,000. Given the amount of uranium in a mineral the amount of radium can be computed from this ratio U : Ra=$3{\cdot}4\times10^{-7}$. This approximate constancy is clearly the result of an equilibrium between production and decay. The supply of radium is regulated by its relative rates of formation and degradation ; and when the speeds of the opposing reactions are balanced, the ratio radium : uranium must be constant. It is interesting to observe in this connection radium has been shown to be a disintegration product of the radioactive elements—*vide supra ;* and that a very small amount of helium is always found occluded in uraniferous minerals. This subject has been investigated by R. J. Strutt, B. B. Boltwood, E. Rutherford, J. A. Gray, R. J. Moss, M. S. Curie, etc. Assuming that no helium escapes, the small amount found in a given rock will be a measure of the time which has elapsed since the birth of that particular sample, but this gas must be constantly leaking into the atm., and, consequently, the age so computed will be a minimum age of the mineral, for the mineral may be older, but not younger than the age so computed. Hence, by determining the relative amounts of uranium and helium in a mineral, its minimum age can be estimated. In this way, R. J. Strutt estimated that it requires eleven million years to produce one c.c. of helium per gram of uranium.

Under ordinary conditions, uranium and all its salts—presumably freed from radium—are radioactive ; the freshly prepared uranium products give only α-rays, but β-rays are slowly developed, and increase up to an equilibrium value which is attained in 6 to 12 months. Some γ-rays are also given off. W. Crookes [2] showed that uranium could be prepared photographically inactive, and the whole of the activity concentrated in a small residue free from uranium, by precipitating a soln. of a uranium salt with ammonium carbonate. On dissolving the precipitate in an excess of the reagent, an insoluble residue remained. This was filtered off, and was found to be many hundreds of times more active photographically than the uranium from which it had been separated. It contained a small quantity of what was called **uranium-X** to distinguish it from uranium or uranium proper. F. Soddy and A. S. Russell say that the success of W. Crookes' process depends on the presence of small quantities of iron and aluminium, for the uranium-X attaches itself to the insoluble impurities. If highly purified uranium be employed, it is best to add a little ferric salt so as to fix the uranium-X. This process was also used by H. Schlundt and R. B. Moore, and by O. Hahn and L. Meitner. S. J. Lloyd separated the uranium-X from the iron, by dissolving the insoluble mass in conc. hydrochloric acid, and extracting the soln. with ether sat. with hydrogen chloride. The uranium-X remains in the aq. layer. In the ammonium carbonate process, F. Soddy recommended dissolving the precipitate in acid, and pouring the soln. into very conc. aq. ammonium carbonate. The soln. can be fractionally precipitated by boiling. According to the nature of the impurities, the uranium-X comes down sharply and definitely with one of the fractions, usually in the middle of the series. Uranium freed from uranium-X emits only α-rays ; uranium-X is responsible for the β- and γ-rays.

T. Godlewsky found that the nitrate of uranium-X is more soluble in water than that of uranium, $UO_2(NO_3)_2.6H_2O$, so that on crystallization uranium-X gradually accumulates in the mother liquid. Hence, if a layer of crystals of the nitrate be heated and allowed to cool slowly, crystallization begins at the bottom, and the uranium-X accumulates in the surface layers. In the course of time, the uranium-X gradually diffuses from the surface layers, and becomes uniformly distributed. This accounts for the anomalous changes in the β-ray activity of uranium observed by S. Meyer and E. von Schweidler. This method of isolating uranium-X was employed by F. Soddy and A. S. Russell, and B. Szilard ; they found that if a hot soln. of sp. gr. 2·05 be allowed to cool, about two-thirds of the salt crystallizes out, and the mother liquid contains about six-sevenths of the total uranium-X. The uranium-X can thus be rapidly conc. by successive crystallizations.

According to W. Crookes, if crystals of uranium nitrate be shaken with aq.

ethyl ether, the lower aq. layer contains uranium which gives the α- and the β-rays; while the upper ethereal layer contains uranium which gives the α-radiations only. Uranium-X thus accumulates in the aq. layer. The extracted uranium regains its power of emitting β-rays and attains a maximum in 6–12 months. A second quantity of uranium-X can be extracted from restored uranium, and so also a third and fourth extraction can be made; and, so far as we can guess, the extraction, restoration, and re-extraction can be repeated an indefinite number of times, that is, until all the uranium has been transformed into uranium-X. Hence, it seems impossible to avoid the inference that **uranium is continuously and spontaneously decomposing into uranium-X and α-particles of helium.** R. B. Moore and H. Schlundt, and V. F. Hess, employed a number of solvents—methyl or ethyl ether; acetone; methyl, ethyl, or amyl alcohol; or methyl or ethyl acetate. They said that acetone and methyl acetate gave the best results; and that the solvents work better if a little iron salt is mixed with the uranium salt. O. H. Göhring combined the ammonium carbonate and the ether processes.

500 grms. of freshly powdered uranyl nitrate was dissolved in 500–600 c.c. of ether; the aq. layer contained the uranium-X and was separated from the ethereal layer by a separating funnel. $\frac{1}{2}N$-ammonium carbonate was added to the aq. soln. until a precipitate was formed. The precipitate was dissolved in an excess of the ammonium carbonate soln. The insoluble iron or thorium hydroxide was allowed to stand an hour, and filtered from the uranium soln. The whole operation occupies about 2 hrs., and the yield of uranium-X is about 98 per cent.

H. Becquerel, and M. Levin showed that uranium-X is entrained with barium or calcium sulphate precipitated in the soln.; and H. Becquerel, M. Levin, V. F. Hess, and A. Ritzel found that when the uranium salt soln. is boiled with animal charcoal, or soot obtained by burning naphthalene, the uranium-X is adsorbed by the solid; and the carbon can then be removed by ignition. According to A. Ritzel, if a thorium salt be present, the uranium-X cannot be separated therefore by charcoal —presumably thorium and uranium-X are physically and chemically isotopic. A. Ritzel showed that there is a definite equilibrium constant in the partition of the uranium-X in the soln. and in the solid; and A. J. Berry obtained an analogous result with barium sulphate in place of carbon. A. C. Brown found the adsorption of uranium-X by basic ferric acetate is proportional to the conc. A. Fleck discussed the isotopy of uranium-X, thorium, and radicactinium.

B. Keetmann added thorium to the uranium soln. and precipitated the acid soln. of uranium-X and thorium as fluorides by adding hydrofluoric acid. G. N. Antonoff added a lanthanum salt in place of a thorium salt, and afterwards precipitated the latter with sodium thiosulphate. A. Ritzel also recommended separating uranium-X by adding some sodium phosphate to the strongly acid soln., and neutralizing with dil. sodium hydroxide. A part of the uranium gradually separates as phosphate, which contains all the uranium-X. The phosphate is dissolved in sulphuric acid, some cerium salt is added, and then hydrofluoric acid. The uranium-X is precipitated with the fluorides. K. Fajans and O. H. Göhring obtained good results with this process.

O. Hönigschmid recommended purifying uranium from other radioactive substances by adding thorium nitrate to a soln. of uranium nitrate in nitric acid, and precipitating with oxalic acid. The filtrate is then evaporated to dryness, and the oxalate decomposed by calcination. The resulting oxide is dissolved in nitric acid, mixed with lead and bismuth nitrate and treated with hydrogen sulphide. The filtrate is then purified by adding a barium salt and precipitating the barium as sulphate. The thorium oxalate precipitation removes radiothorium, ionium, actinium, radio-actinium, and uranium-X; the lead and bismuth sulphide removes the radio-lead and polonium; and the barium sulphate precipitation removes radium, mesothorium, thorium-X, actinium-X, and uranium-X. The process has been discussed by F. Soddy and T. D. Mackenzie, G. N. Antonoff, and S. Meyer and F. Paneth.

Uranium freed from uranium-X emits only α-particles. H. Geiger and E. Rutherford found that each gram of uranium emitted $2{\cdot}37\times10^4$ α-particles per second,

while a gram of a mineral in radioactive equilibrium emitted $9{\cdot}6\times10^4$ particles per second. They therefore inferred that the decay of the uranium atom is attended with the emission of two α-particles. H. N. McCoy and W. H. Ross, and B. B. Boltwood also concluded that two α-particles are emitted by uranium for one by radium or ionium. E. Marsden and T. Barratt found that it is very unlikely that the uranium atom emits two α-particles simultaneously, because no sign of doubles was observed by the scintillations method; rather was it inferred that the uranium breaks into two distinct substances in equilibrium each one of which breaks up with the emission of one α-particle. Experiments were made by A. Foch, and F. Friedmann; while H. Geiger and J. M. Nuttall showed that two groups of α-rays are emitted from uranium at 15°, one, of range 2·5 cms. and velocity $1{\cdot}37\times10^9$ cms. per sec., is emitted by say **uranium-I**—at. wt., 238·5; and the other of range 2·9 cms. and velocity $1{\cdot}44\times10^9$ cms. per sec., is emitted by **uranium-II**—at. wt., 234·5. Hence, **uranium freed from uranium-X is a complex containing two components which emit α-rays.** No success has attended the efforts to separate these components by chemical treatment. H. Geiger and F. Rutherford, S. Meyer, H. N. McCoy, and M. S. Curie have deduced that the half-value period of uranium-I is $4{\cdot}8\times10^9$ yrs.; the average life period is $7{\cdot}2\times10^9$ yrs.; and the radioactive constant $\lambda=1{\cdot}4\times10^{-10}$ yrs. or $4{\cdot}4\times10^{-18}$ secs.; while for uranium-II, the half-life period is approximately 2×10^6 yrs.; the average-life period, 3×10^6 yrs.; and the radioactive constant $\lambda=3\times10^{-7}$ yrs. or 10^{-14} secs. Uranium-II is the parent of ionium, and is descended from uranium-X_2.

Uranium-X has an at. wt. 230·5; it emits β-rays; and, as shown by A. S. Eve, and F. Soddy, it also emits feeble γ-rays which have a penetrating power not much less than the γ-rays of radium. The absorption coeff. of the γ-rays for lead is 0·725; for glass, 0·122; for magnesite, 0·0917; for sulphur, 0·0921; and for paraffin wax, 0·0433. H. Richardson found for aluminium 0·70 cm.$^{-1}$, and 0·140 cm.$^{-1}$. H. W. Schmidt found that the β-rays are fairly penetrating and have an absorption coeff. 15 cms.$^{-1}$ for aluminium; it also emits some soft β-rays with an aluminium absorption coeff. of 510 cms.$^{-1}$. The ionization produced by the soft β-rays was at first ascribed to the emission of some α-rays by uranium-X, but M. Levin showed that this interpretation was wrong. L. Meitner studied the β-rays of uranium-X and showed that their velocity is 95 per cent. of that of light. Uranium-X has not been volatilized. Uranium-X loses its activity in the course of a few months; the loss follows the exponential law. This has been investigated by E. Rutherford and F. Soddy, F. Soddy and A. S. Russell, S. Meyer and E. von Schweidler, V. F. Hess, and G. N. Antonoff, who find that the half-life period is nearly 24·6 days; the average-life period, 35·5 days; and the radioactive constant, $\gamma=0{\cdot}0282$ day.

The two sets of β-rays—hard and soft—expelled by uranium-X were shown by K. Fajans and O. H. Göhring to be produced by two consecutive changes, and not by a single change. The two products cannot be separated by recoil, but they can be resolved by chemical and electrochemical methods. F. Soddy and J. A. Cranston found that when a preparation of uranium-X is heated in a current of air and carbon tetrachloride vapour uranium-X_2 is readily volatilized from uranium-X_1. Both components emit β-rays and γ-rays—the velocity of the β-rays of the one, called **uranium-X_1,** is $1{\cdot}44\times10^{10}$ to $1{\cdot}77\times10^{10}$ cms. per sec., and the velocity of the β-rays of the other, called **uranium-X_2,** is $2{\cdot}46\times10^{10}$ to $2{\cdot}88\times10^{10}$ cms. per sec. The half-life period of uranium-X_2 is 23·5 days; the average-life period, 33·9 days; and the radioactive constant, $\gamma=0{\cdot}0295$ day or $3{\cdot}41\times10^{-7}$ secs. The half-life period of uranium-X_2 is 1·17 mins.; the average-life period 1·69 mins.; and the radioactive constant, $\lambda=0{\cdot}59$ min., or $9{\cdot}9\times10^{-4}$ secs. These results were confirmed by O. Hahn and L. Meitner, G. N. Antonoff, and by A. Fleck. The absorption coeff. of the hard β-rays from uranium-X_2 is 15 cms.$^{-1}$ of aluminium; and that of the soft β-rays from uranium-X_2 is 500 cms.$^{-1}$ of aluminium. H. Richardson attributed the harder γ-rays, with an absorption coeff. of 0·14 cm.$^{-1}$ of aluminium,

to uranium-X_2; and the softer γ-rays, with an absorption coeff. of 24 and 0·70 cms.$^{-1}$ of aluminium, to uranium-X_1. G. von Hevesy gave 0·40 sq. cm. per day for the diffusion constant of uranium-X_2, and said that it corresponded with a quadrivalent element. Uranium-X_2 is a nobler element than uranium-X_1, *i.e.* the former deposits on metals more readily than the latter. The closest chemical relation of uranium-X_2 is tantalum, while uranium-X_2 is isotopic with thorium. Uranium-X_2 occupies the vacant place in the periodic table corresponding with *ekatantalum;* it therefore constitutes a distinct chemical type, and its discoverers propose to call it **brevium,** symbol Bv, in reference to its short life. G. von Hevesy, and A. S. Russell interpret the sequence of the decay products so far considered as uranium-I→ uranium-X_1→uranium-X_2→uranium-II→ . . . The parent of uranium-X_1 is therefore uranium-I, and that of uranium-X_2, is uranium-X_1; the decay of uranium-X_1 furnishes uranium-X_2; and the decay of uranium-X_2 furnishes uranium-II.

The separation of uranium-X_1 from uranium-X_2 was discussed by O. H. Göhring and K. Fajans. Uranium-X_2 is so short-lived that not more than a couple of minutes should elapse between its first precipitation and its exposure to the electroscope. The first method rests on the electronegative character of uranium-X_2. A feebly acid soln. of uranium-X containing some iron salt was poured into a clean lead capsule, stirred for a minute, and the soln. poured off. The capsule was rapidly washed with alcohol and ether. The deposit of uranium-X_2 can then be tested with an electroscope. A second method rests on the analogy between uranium-X_2 and tantalum, and uranium-X_1 and thorium. If a soln. of tantaliferous uranium-X_2 be tested with a reagent which precipitates tantalum, but not thorium, the tantalum will retain the uranium-X_2 while the uranium-X_1 will remain in soln. O. H. Göhring and K. Fajans precipitated tantalum as hydrated tantalic acid from neutral or feebly acid soln. containing potassium hexatantalate. The mixture was filtered, washed by suction, and dried over a hot porous tile. The precipitate retains less than 0·2 per cent. of uranium-X_1. O. Hahn and L. Meitner proceed as follows:

> The mother liquid remaining after the crystallization of uranyl nitrate three times was poured into an excess of a soln. of ammonium carbonate. The uranium-X was dissolved in acid, and filtered. A few milligrams of tantalic acid was boiled in water and poured over the uranium-X on the filter. The product was simply dried, or washed and dried. The product was then tested with the electroscope. If a feebly acid soln. be used, a relatively large proportion of uranium-X_1 is retained; while with conc. acid less uranium-X_2 is obtained on account of its solubility in the acid.

If a soln. containing uranium-X_2, an iron salt, and potassium fluorotantalate be treated with a sat. soln. of potassium sulphate, a flocculent precipitate containing the uranium-X_2 is obtained. If silver nitrate be added to a dil. acetic acid soln. of uranium-X containing iron or thorium, and heated, the precipitated silver retains the uranium-X_2. If hydrofluoric acid or ammonium fluoride be added to a soln. of uranium-X containing some thorium, the uranium-X_1 will be precipitated with the thorium fluoride, while the uranium-X_2 remains in soln.

S. Meyer and E. von Schweidler, H. Becquerel, and F. Soddy obtained evidence of the association of a short-lived product with uranium-X. G. N. Antonoff found that the decay curve of uranium-X depended on whether it had been separated by precipitating barium sulphate in the uranium salt soln., or by adding a ferric salt and boiling. The decay curve of the former, with either the hard or soft β-rays, was exponential for a period of 24 days, while that of the latter, with the soft β-rays, was faster than normal for the first few days; while if the soft β-rays were screened off, the decay curve was normal. It was therefore inferred that the precipitated ferric hydroxide absorbs a short-lived product, called **uranium-Y,** which is not present in the precipitated barium sulphate. Uranium-Y has been also studied by A. Fleck, A. Piccard and E. Stahel, F. Soddy, O. Hahn and L. Meitner, and E. Rona. The at. wt. is given as 230·5. It was inferred from the decay curve that its half-life period is 25·5 hrs.; its average-life period is 36·8 hrs.; and its radioactive constant λ=0·46 day, $2{\cdot}72\times10^{-2}$ hrs., or $7{\cdot}55\times10^{-6}$ secs. It emits soft β-rays, for which the

absorption coeff. is 300 cms.$^{-1}$, and some for which the absorption coeff. is 2500 cms.$^{-1}$. There is a little evidence of the emission of a very small proportion of α-rays. Uranium-Y is isotopic with uranium-X_1, and is thought by some to be progenitor of the actinium series of radioactive elements. The increase in the activity of uranium freed from uranium-X showed that uranium-Y could not be parent of uranium-X; and the fact that the amount of uranium-Y was independent of the age of the uranium preparation showed that it was not produced by uranium-X. Hence, it is inferred that uranium-Y is a side branch product concurrently formed, in exceedingly minute proportion, with uranium-X, or ionium, Io. The descent is either

$$U_1 \begin{cases} \rightarrow U_Y \rightarrow ? \\ \rightarrow U_{X_1} \rightarrow U_{X_2} \rightarrow U_{II} \rightarrow Io \rightarrow \ldots \end{cases}; \quad \text{or,} \quad U_1 \rightarrow U_{X_1} \rightarrow U_{X_2} \rightarrow U_{II} \begin{cases} \rightarrow U_Y \rightarrow ? \\ \rightarrow Io \rightarrow \ldots \end{cases}$$

J. Danne reported yet another product in uranium-X which he called *radio-uranium*, but the report has not been verified, and it is thought to have arisen from observations on imperfectly purified uranium which contains many radioactive substances. A. Piccard and E. Stahel reported a substance *uranium-V* to be the source of the soft radiations emitted by uranium-X, but O. Hahn showed that the effect is possibly due to the existence of uranium-V.

A genetic connection between uranium and radium is so strongly indicated by the constancy of the U : Ra ratio in minerals, that a search was made for an immediate parent of radium. E. Rutherford and F. Soddy [3] originally suggested that uranium is the primary source of radium, but the last-named found that the rate of production of radium in soln. of uranium nitrate, freed from uranium-X, was a thousand times smaller than would obtain if the uranium passed directly into radium. B. B. Boltwood likewise detected no growth of radium, over a period of 390 days, in a soln. containing 100 grms. of purified uranium nitrate. These results showed that uranium does not change directly into radium, but that an unknown product of slow transformation occurs as an intermediate product in the passage of uranium to radium. B. B. Boltwood at first concluded that actinium was the missing intermediate product because the radium content of a sample derived from carnotite increased by $8{\cdot}5 \times 10^{-1}$ grms. in 193 days. E. Rutherford, however, found that while some samples of actinium behaved like B. B. Boltwood's specimen, other samples did not grow radium to an appreciable extent. It was therefore concluded that the parent of radium was not actinium itself, but rather an unrecognized radioactive component present in actinium. B. B. Boltwood named this product **ionium**, Io. He found that the ionium followed the actinium in the separation from the uranium minerals. Actinium and ionium can be separated. Nearly all uranium minerals contain some thorium, but neither B. B. Boltwood nor B. Keetman were able to separate ionium from thorium. The two elements cannot be separated by the fractional sublimation of the acetylacetones, and it is doubtful if ionium has been obtained free from thorium. The only way to get ionium free from that element is to find a mineral containing no thorium. F. Soddy added:

> Its chemistry can be fully and accurately described in a single sentence. It resembles thorium in its whole nature, as far as it is known, with absolute completeness, so that not only is no separation of the two elements possible by any known method, but no concentration of the one constituent with reference to the other has been accomplished. Such an alteration of concentration could be readily detected, if it occurred, even with the infinitesimal amounts of ionium used, because of the intense α-activity of the latter. Thorium and ionium form a pair of non-separable elements. Radio-thorium, certainly, and, according to some authorities, uranium-X, are also non-separable from thorium. This apparently complete chemical identity of different elements of, in some cases, different at. wt., is one of the most important results of the study of radioactivity, and many other examples will occur. It must be remembered that the chemistry of thorium has been closely and exhaustively studied on account of its resemblance to and association with many other rare earths of no technical value, and in consequence a large number of characteristic and effective methods for the purification of thorium from all other elements are known.

In working the uranium ores for radium by the processes of M. S. Curie, L. Haitinger and C. Ulrich, etc., the ionium will be found with the rare earths. The usual

method of separating thorium from minerals is to add a thorium salt, except with minerals definitely thoriferous, and then proceed to precipitate the thorium by the standard methods—*e.g.* with sodium thiosulphate, ammonium carbonate, oxalic acid, or hydrofluoric acid The ionium follows the thorium. The radioactivity of thorium is much smaller than that of ionium. Cerium salts have been used in place of thorium, the ionium follows the cerium ; and the cerium can be separated from the ionium by the standard methods for separating cerium from thorium. B. Keetman used aluminium salts in place of thorium salts. C. A. von Welsbach removed lead, etc., by adding sulphuric acid to a nitric acid soln. of pitchblende ; he then precipitated the fluorides, and fractionally precipitated the soln. of the fluorides in boiling sulphuric acid by means of zinc hydroxide slurry. The first precipitate contained all the thorium and ionium. B. Keetman said : If not too great an excess of zinc hydroxide be employed, the last traces of ionium can be separated from the rare earths ; but a repetition of the process is necessary or the product will be contaminated with some cerium and didymium. The separation of zinc is effected by treating the acid soln. with ammonia, or soda-lye, or hydrofluoric acid. B. Keetman also found that in the presence of phosphoric acid, soln. of the rare earths are quantitatively precipitated as fluorides, lead and calcium fluorides are also precipitated, while uranium, iron, etc., remain in soln. He recommended the following process for separating ionium from uranium minerals :

> The uranium ore was dissolved in warm dil. nitric acid, and the soln. evaporated to dryness to make the silica insoluble. The mass was digested with dil. nitric acid, and the filtrate evaporated with sulphuric acid to convert the nitrates to sulphates. When the soln. is diluted with water, barium, radium, and lead sulphates are precipitated. The filtrate was then boiled with hydrofluoric acid in a platinum dish. The precipitated fluorides were collected on a filter, again decomposed by heating with sulphuric acid, and then dissolved in water. Oxalic acid was added, and the precipitate digested with a hot conc. soln. of ammonium oxalate, and diluted with water. The yttria earth-oxalates are filtered off, the soln. containing thorium and ionium. The oxalates are precipitated by adding hydrochloric acid. B. Keetman obtained 0·1 grm. of very radioactive thorium oxalate from 200 grms. of African pitchblende.

H. M. Plum has described the separation of ionium from carnotite. E. Rona estimated the ionium content of various radium residues. B. B. Boltwood found that the amount of ionium in a number of minerals was proportional to the amount of uranium ; and rate of production of radium was proportional to the amount of ionium. Ionium and radium are separated by adding barium chloride to the sulphuric soln., radium sulphate precipitates with the barium sulphate, and uranium remains in the filtrate. In course of time, however, radium re-forms in the ionium soln. Radium was generated from ionium at a constant rate over the period of measurement—500 days. The slow growth of radium in soln. of uranium salts observed by F. Soddy was due to the small quantity of ionium initially present ; F. Soddy and T. D. Mackenzie found no detectable growth of radium in uranium soln. from which the ionium had been previously separated, but radium did grow in soln. of ordinary uranyl nitrate which contain ionium. Hence, too, as O. Hahn has shown, all thorium preparations containing ionium will generate radium—in minute quantities. Uranium-II is thought to be the parent of ionium, and ionium the parent of radium.

The at. wt. of ionium is estimated to be about 230. F. Exner and E. Haschek, A. S. Russell and R. Rossi, and O. Hönigschmid examined the spectrum of thorium-ionium preparations estimated to contain 10 per cent. of ionium ; the spectral lines of thorium were obtained, but not a single line that could be attributed to ionium. The radioactivity of ionium resembles that of polonium. According to B. B. Boltwood, L. P. Wheeler and T. S. Taylor, S. Meyer and co-workers, B. Keetman, and E. Rutherford, it emits α-rays of range of about 3 cms. at 15° and of initial velocity $1{\cdot}46 \times 10^9$ cms. per sec. B. B. Boltwood observed a transient β-ray activity which decayed in 22 days, indicating that it was produced by uranium-X which had been separated with the ionium. J. Chadwick and A. S. Russell found that ionium

purified from the radioactive bodies which emit β- and γ-rays, emitted a small but easily detectable amount of γ-radiation. This radiation is shown to be excited by the α-rays, either in the ionium itself or in the thorium with which it is mixed. It is a mixture of three types of radiation differing widely in penetrating power. The absorption coeff. divided by the sp. gr. of aluminium are respectively 400, 8·4, and 0·15 cms.$^{-1}$. Estimates have been made of the life of ionium by F. Soddy, B. B. Boltwood, and H. Geiger and J. M. Nuttall; the best representative values are 2×10^5 yrs. for the half-life period, and $3{\cdot}5\times10^5$ yrs. for the average-life period. According to F. Soddy:

> Ionium possesses the great advantage over polonium for many purposes, in that its radioactivity is constant and does not sensibly decay. It will no doubt find large application where a steady, powerful source of α-radiation is required, as in compensation methods of radioactive measurement and for α-ray standards more active than those of uranium. The proportion changing into radium, even in a lifetime, is so small that it may in most cases be neglected. It is only by refined emanation tests that it can be detected.

Table V gives a summary of the radioactive properties of the uranium radium family. A new radioactive substance, designated *uranium-Z* until its parentage is definitely elucidated, and having the chemical properties of protactinium, was shown by O. Hahn to be present in ordinary uranium salts. It emits β-radiations, and has a half-life period of 6·7 hrs. Under the prescribed conditions the intensity of radiation of the new substance is only about 0·25 per cent. of that of uranium-X, that is, a mixture of uranium-X_1 and -X_2, obtained from the same quantity of uranium. The parent substance can be only uranium-X_1, or a new isotope of similar life-period.

TABLE V.—SUMMARY OF RADIOACTIVE CONSTANTS OF THE URANIUM-RADIUM SERIES.

	At. wt.	Half-life Period.	Radioactive constant, λ.	Rays.	Velocity α-rays cm./sec.	Velocity β-rays (Light unity).
Uranium-I	238·2	5×10^9 yrs.	$4{\cdot}3\times10^{-18}$	α	$1{\cdot}36\times10^9$	—
Uranium-X_1	234·2	23·5 d.	$3{\cdot}3\times10^{-7}$	β, γ	—	wide range
Uranium-X_2	234·2	1·7 min.	0·01	β, γ	—	0·52, 0·65
Uranium-II	234·2	2×10^6 yrs.	$1{\cdot}1\times10^{-14}$	α	$1{\cdot}44\times10^9$	—
Uranium-Y	230·2	25·5 hrs.	$7{\cdot}5\times10^{-6}$	β	—	—
Ionium	230·2	10^5 yrs.	$2{\cdot}2\times10^{-13}$	α	$1{\cdot}47\times10^9$	—
Radium	226	1730 yrs.	$1{\cdot}26\times10^{-11}$	α, β	$1{\cdot}50\times10^9$	—
Ra Emanation	222	3·85 d.	$2{\cdot}08\times10^{-6}$	α	$1{\cdot}62\times10^9$	—
Radium-A	218	3·0 mins.	$3{\cdot}85\times10^{-3}$	α'	$1{\cdot}70\times10^9$	—
Radium-B	214	26·8 mins.	$4{\cdot}33\times10^{-4}$	β, γ	—	0·36 to 0·74
Radium-C_1	214	19·5 mins.	$5{\cdot}93\times10^{-4}$	α, β, γ	$1{\cdot}92\times10^9$	0·80 to 0·98
Radium-C_2	210 ?	1·4 mins.	$8{\cdot}3\times10^{-3}$	β	—	—
Radium-C′	210	10^{-6} sec. ?	$7\times10^{+5}$	α	—	—
Radium-D	210	16·5 yrs.	$1{\cdot}39\times10^{-9}$	β	—	0·33, 0·39
Radium-E	210	5·0 d.	$1{\cdot}66\times10^{-6}$	β, γ	—	wide range
Polonium (RaF)	210	136 d.	$5{\cdot}90\times10^{-8}$	α	$1{\cdot}58\times10^9$	—

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§ 11. The Descendants of Uranium and Radium

The habit of suspending judgment until the conclusion has been fully tested by varying the circumstances of the experiment, and by repeated accurate measurement, is a valuable habit to acquire.—G. F. Fitzgerald.

It is assumed that the element uranium, after a long series of transformations, passes into a form of matter which has no radioactivity or a radioactivity too feeble to be detected by available methods. The successive stages are summarized in Table VI, where the at. wt., the nature of the radiations, and the half-life period are indicated. The side branches involving uranium-Y and radium-C_2 have been

omitted. The radioactivity of aged uranium is therefore a complex quality because of the presence of the decay products. B. B. Boltwood has estimated that if the radioactivity of uranium as oxide be unity, the relative activities of the various products in the mineral uraninite are :

Io	Ra	Nt	Ra_A	Ra_B	Ra_C	Po or Ra_F	Ac products
0·34	0·45	0·62	0·54	0·04	0·91	0·46	0·28

so that the total activity of the mineral is 4·64 times that of the contained uranium ; and a gram of radium freed from all products has the activity of 1,300,000 grms. of uranium. The subject has also been studied by H. N. McCoy and W. H. Ross. L. Meitner discussed the mechanism of the radioactive disintegration of the elements.

TABLE VI.—GENEALOGICAL TREE OF THE URANIUM-RADIUM FAMILY.

α-rays	(5×10^{19} years)	**Uranium-I** (238·18)
β- and γ-rays	(23·5 days)	Uranium-X_1 (234·18)
β- and γ-rays	(1·7 mins.)	Uranium-X_2 (234·18)
	(2×10^6 years)	Uranium-II (234·18)
α-rays	(1×10^5 years)	Ionium (230·18)
α- and β-rays	(1730·375 years)	Radium (226)
α-rays	(3·85 days)	Emanation (222)
α-rays	(3·0 mins.)	Radium-A (218)
β- and γ-rays	(26·8 mins.)	Radium-B (214)
β- and γ-rays	(19·5 mins.)	Radium-C_1 (214)
β-rays	(16·5 years)	Radium-D (210)
β- and γ-rays	(5·0 years)	Radium-E (210)
α-rays	(136 days)	Radium-F (210)
α-rays		Radium-G (206)

The alternative name for uranium-X_2 is *brevium ;* for radium emanation, *niton ;* and for radium-F, *polonium.* Radium emanation is preferred by physicists, chemists often use niton. M. C. Neuburger has discussed the nomenclature of radiochemical transformations. There are facts which support B. B. Boltwood's hypothesis [1] that radium-G is lead. The evidence that polonium passes spontaneously into lead is at present purely circumstantial. W. R. Gray reported that he found lead in some capillary tubes in which a minute quantity of radium emanation had been stored for four years. There are three possible sources of the lead : (*a*) the glass of the tubes contained 0·03 per cent. of lead ; (*b*) the mercury used to seal the tubes contained a trace of lead ; (*c*) the disintegration of the emanation, *à la* the emanation hypothesis. The glass of the tube was undoubtedly attacked by the emanation as shown by the discoloration, although no measurable amount of lead was obtained by digesting the powdered glass with water for some time. The alleged generation of lead is thought to be due to the confusing of isotopic radium-D with lead.

K. Fajans and H. Towara suggested that a *radium-H* is formed from radium-G by the emission of β-rays, and that radium-H gives off α-rays producing an isotope of thallium. This would account for the presence of thallium and bismuth in pitchblende. The range of the α-particles was about 3 cms., the half-life period is between 10^5 and 10^6 yrs. L. Meitner, and O. Hönigschmid have discussed this subject.

It has been argued that if the end-products of the radioactive transformations are stable and non-volatile, these products must be accumulating in the radioactive minerals. The amount of the end-product in the unaltered mineral would be expected to depend on the amount of the parent element originally present, and on the age of the mineral. B. B. Boltwood examined a number of old unaltered minerals, and was led to suggest that lead is the end-product of the uranium-radium series, because the ratio Pb : U is nearly constant for unaltered minerals from the same locality, and presumably the same geological age, but the ratio varies with minerals from different localities. For example, five uraninites from Glastonbury (Conn.) had a ratio 0·041 ; five from Branchville had the ratio 0·053 ; one from Texas, 0·170 ; thorianite from Ceylon had a ratio 0·20 ; a group of minerals from Norway had the ratio 0·125, and another group, 0·155. A. Holmes also extended the observations and found the ratio to be unaffected by the presence of thorium, showing that this element is not genetically related with lead. The decay of uranium is attended by the expulsion of eight α-particles, *i.e.* eight atoms of helium ; it follows that the amount of the assumed lead—at. wt. 238·18, minus $8\times3{\cdot}994=206{\cdot}3$—formed per gram or uranium per year is $1{\cdot}25\times10^{-10}$ grms. Hence, assuming that the rate of production of lead has remained constant, the maximum age of a mineral will be $Pb/1{\cdot}25\times10^{-10}U$, or $8\times10^9 Pb/U$ yrs. A. Holmes gives the results indicated in Table VII. The estimate represents maximum values because of the

Table VII.—Ratio of Lead to Uranium in Minerals.

Geological Period of Mineral.	$\frac{Pb}{U}$	Age in millions of years.
Carboniferous	0·041	340
Devonian	0·045	370
Pre-Carboniferous	0·050	410
Silurian or Ordovician	0·053	430
Pre-Cambrian—Sweden	0·125–0·155	1025–1270
United States	0·160–0·175	1310–1435
Ceylon	0·200	1640

possibility of some of the lead having been deposited with the minerals first, and estimations based on the occluded helium represent minimum values because a part of the gas must have escaped.

According to O. Hönigschmid, the at. wt. of uranium is not less than 238·08, and not greater than 238·18. If lead is formed by the loss of eight atoms of helium, at. wt. 3·994, the computed value for the at. wt. is 206·23 ; the at. wt. of ordinary lead is 207·20. Similarly, if lead is formed from radium, at. wt. 226, by the loss of five α-particles, the at. wt. should be 206·03. Lead derived from an analogous series of radioactive transformations is computed by K. Fajans and F. Soddy to have an at. wt. 208·4. The discrepancy attracted attention to the possibility that lead from uranium earths may not have the same at. wt. as ordinary lead. F. Soddy and H. Hyman tried if the at. wt. of lead extracted from the mineral thorite and ordinary lead showed any difference. They reported that the former gave the larger result, though no special precautions were taken to eliminate silver. The at. wt. of thorite lead being 208·3–208·5 ; M. Curie similarly found that lead derived from monazite had an at. wt. 207·08 ; that from pitchblende, 206·5 ; that from galena, 207·01. T. W. Richards and M. E. Lembert found lead derived from uraninite of Carolina had an at. wt. 206·40 ; that from pitchblende of Joachimsthal, 206·37 ; that from carnotite of Colorado, 206·59 ; that from thorianite of Ceylon,

206·82; that from pitchblende of Cornwall, 206·86; and that from commercial lead, 207·15. T. W. Richards and C. Wadsworth extended these observations to lead obtained from various radioactive minerals. Confirmatory observations were made by T. W. Richards and J. Sameshima, T. W. Richards and W. C. Schumb, O. Hönigschmid and S. Horovitz, A. L. Davis, M. Muguet, and K. Fajans. Hence, it has been inferred that "there are several varieties of lead of different at. wt. determined by the element from which they are derived." In general, **lead derived from radioactive minerals has a different atomic weight from ordinary galenic lead.** T. W. Richards added:

> The inference seems to be that radioactive lead contains an admixture of some substance different from ordinary lead, and very difficult to separate from it by chemical means. This substance cannot be identified in the ultra-violet spectrum of the material, either because it has the same spectrum as lead, or because it has no spectrum in that part of the field, or because its spectrum is masked or absorbed by that of lead.

The spectra of the different specimens of lead have been examined by T. W. Richards and co-workers, F. Soddy and H. Hyman, F. Haschek, and O. Hönigschmid and S. Horovitz, from which it is concluded that the spectra of lead derived from radium, and from *plumbum commune*, both in the visible and ultra-violet regions, with λ between 2380 and 4470, are identical. T. W. Richards and C. Wadsworth showed that *plumbum commune*, at. wt. 207·2, had a sp. gr. 11·337 at 19·94, whereas a sample of Australian radioactive lead, at. wt. 206·3, had a sp. gr. 11·288. The two samples thus had virtually the same at. vol. 18·276 and 18·277.

The expulsion of an α-particle from an atom lowers the at. wt. of the original atom by 3·994, say 4, the at. wt. of helium. Thus, the at. wt. of radium is 226, that of niton 224, and that of helium 4. It follows, therefore, that radium→niton +helium. The assumption is employed in estimating the at. wt. of the other radioactive substances. The emission of β-rays, *i.e.* electrons, is supposed to produce no measurable change in the at. wt., while the emission of α-rays (charged helium atoms) at each stage of the disintegration is supposed to reduce the at. wt. by 4. F. Soddy pointed out that the expulsion of an α-particle by a radioactive element causes the residual product to shift its position two places in the periodic table in the direction of diminishing mass, so that the residual product is not in the next family, but in the next but one. This reduces the valency of the element by 2. For example, sexivalent uranium loses an α-particle to form uranium-X, isotopic with thorium, and therefore quadrivalent; quadrivalent ionium loses an α-particle, forming bivalent radium; and the latter loses an α-particle to form nullvalent niton. A. S. Russell[2] expressed the **displacement rule:** *whenever an α-particle is expelled by a radioactive element the group in the periodic table, to which the resultant product belongs, is either two units greater or two units less than that to which the parent belongs.* Similarly, *when an element gives off a β-particle with or without the accompaniment of γ-rays, the resultant product shifts its position so that it is one unit greater or one unit less than that to which the parent belongs.* Hence, two changes attended by the emission of β-particles, and one by an α-particle, could bring the product back to its original position in the periodic table. When a body like radium-C expels both α- and β-rays, the group to which the resultant product belongs may differ from that of the parent by $2 \pm 1 = 1$ or 3. These rules are illustrated by the arrangement, Fig. 15, showing the position of the decay-products of the uranium-radium series in the periodic table. The subject of isotopism has also been discussed by K. Fajans, A. Fleck, F. Paneth, G. von Hevesy, F. Kirchhof, A. van den Broek, S. Meyer, O. Hahn and L. Meitner, I. W. D. Hackh, F. J. Corrigan, M. L. Neuburger, E. Hendrick, R. Brunetti, W. D. Harkins, etc.

F. Soddy postulated that when any number of elements occupy one place in the periodic table, these elements cannot be separated from one another by any known chemical process. Thus, when mesothorium-I gives off two β-particles and

one α-particle to form thorium-X, it is claimed that the two substances cannot be separated from one another in spite of the difference in their at. wts. ; and they are probably spectroscopically indistinguishable. F. Soddy called the non-separable elements **isotopic elements,** or **isotopes**—*ἴσος*, the same ; *τόπος*, a place—because they occupied the same place in the periodic table. K. Fajans suggested the term *pleiadic elements* or *pleiades*—after the small group of stars in the constellation Taurus—*e.g.* ionium, thorium, and radio-thorium are isotopic ; and mesothorium is isotopic with radium. F. W. Aston uses *isobars* as a general name for atoms having

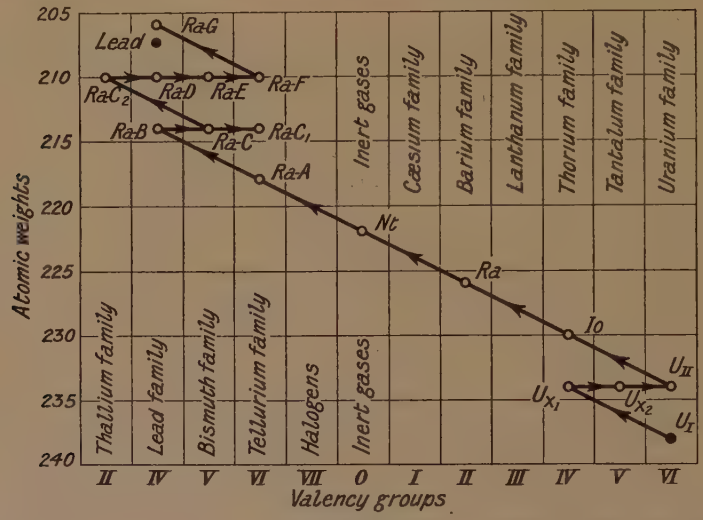

FIG. 15.—Arrangement of the Uranium-Radium Decay Products in the Periodic Table.

the same mass but different chemical properties. F. Sekera has discussed the nomenclature of isotopism. A number of isotopes of non-radioactive elements have been detected by positive ray analysis (*q.v.*). The principle of isotopy is not in conformity with J. Dalton's dogma :

> The ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words, every particle of water is like every other particle of water, and every particle of hydrogen is like every other particle of hydrogen.

The alleged inseparability of the isotopes may be questioned as a reflection on the skill of succeeding chemists. H. S. Shelton maintains that if the atoms of an element be regarded as entities varying about a mean, so must also the properties referred to the atom. In 1888, W. Crookes postulated atoms of variable at. wt., but also assumed a concomitant variation of properties.

The different forms of lead discovered by F. Soddy connected with radio-activity are also said to be isotopic, for they are said to be inseparable, having the same at. vol. and the same chemical and physical properties ; but F. A. Lindemann has shown that two elements of different at. wt. must differ either in their chemical or physical properties. The argument is based on the laws of thermo-dynamics, and was extended in conjunction with F. W. Aston. The subject was discussed by K. Fajans and co-workers, R. A. Mulliken and W. D. Harkins, etc. If the at. vols. are the same, the elastic constant, vap. press., etc., should differ, and it was predicted that the lead from thorite will probably have a m.p. 1·54° higher than ordinary lead. K. Fajans concludes that at absolute zero the at. vols. of isotopes should be the same, and they should differ progressively as the temp. rises ; at ordinary temp. with the lead isotopes, the difference should be less than 0·0001 part. J. Joly and J. H. J. Poole attempted to separate lead isotopes by centrifuging the molten metal, and obtained a negative result. The sp. hts. in the case

of lead isotopes should differ by about 0·75 per cent. S. Chapman, O. Stern and M. Volmer, and E. Kohlweiler discussed fractional diffusion; and R. S. Mulliken and W. D. Harkins showed that isotopes should exhibit differences in their rates of diffusion through porous walls, and in their rates of evaporation into a vacuum. J. N. Bronsted and G. von Hevesy failed to separate mercury isotopes by fractional evaporation. T. W. Richards and N. F. Hall found the β-ray activity of different fractions of isotopic lead were the same. A. Haas discussed the spectroscopy of isotopes; W. D. Harkins and L. Aronberg showed that there must be spectral differences between the spectra and between other properties of isotopes; M. Siegbahn and W. Stenström found the L- and M-series of X-ray spectra of lead isotopes are the same; C. D. and D. Cooksey observed no difference in the high-frequency spectra of lead isotopes. F. W. Loomis showed differences probably occur in the infra-red spectra of the isotopes of chlorine; and T. R. Merton and H. Hartley suggested that by exposing chlorine to light and then to hydrogen, the heavier isotope will react the faster. T. W. Richards and W. C. Schumb found the refractive indices of the crystals of isotopic lead nitrate were the same. T. W. Richards and N. F. Hall found the molar solubilities of the isotopes of lead to be virtually the same because a thousand fractional crystallizations produced no separation. T. W. Richards and W. C. Schumb found no difference in the molar solubilities of the nitrates of common lead and lead from uranium minerals. If the molar solubilities are the same, then, since the mol. wts. are different, the solubilities in grams per litre, and the sp. gr. of sat. soln. ought to show small differences; and K. Fajans and co-workers found the sp. gr. of sat. soln. have the same ratio to the mean sp. gr. as the difference in the at. wt. to the mean at. wt. H. Lachs and co-workers failed to separate uranium-I and -II by fractional diffusion. G. von Hevesy and F. Paneth have established the electrochemical identity, and Z. Klemensiewicz, the electrode potential identity of isotopic elements—within the limits of their methods of measurement. E. Schrödinger discussed the reversible mixing of two gases of different mol. wt., and chemically inert to one another. R. S. Mulliken discussed the separation of isotopes by thermal and press. diffusion; T. Iredale, the possibility of isotopic elements furnishing asymmetric atoms in enantiomorphic compounds. The difference in the series spectra of isotopes was discussed by P. Ehrenfest, N. Bohr, and J. W. Nicholson.

C. T. Kingzett [3] maintained that *isotopism* is another name for *allotropism*, and that isotopes are "atomically or molecularly modified form of one and the same substance, although possibly possessed of distinctive at. numbers or mol. wts." A. Fleck held that the two phenomena are quite distinct, that isotopism refers to a difference in the at. wts. of individual atoms, and that multiples of atoms are not involved.

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§ 12. Actinium and its Putative Parent

In 1899, A. Debierne,[1] while working up uranium residues for M. S. Curie in her quest for the cause of the radioactivity of pitchblende, found that the precipitate obtained by ammonia had a very marked radioactivity. He called the element *actinium*, but said it could not be separated from thorium. Soon afterwards, F. Giesel obtained a radioactive substance from pitchblende; it separated along with the rare earths and was ultimately obtained admixed with lanthanum. He called it *emanium*, and concluded it was not identical with A. Debierne's actinium because emanium was not separated with thorium. Later, A. Debierne found that his preparation emitted an emanation similar to that of F. Giesel's preparation, and it was found that the observation about thorium was wrong. After some controversy, it was agreed that only one radioactive substance was involved, and it was called **actinium,** Ac. E. Rutherford and B. B. Boltwood showed that the original preparations also contained ionium. O. Hahn and O. Sackur established the identity of the emanations of actinium and emanium; and W. Marckwald's claim that the two are not the same substance, but are genetically related with one another, was shown by O. Hahn to be due to the presence of another radioactive substance—radioactinium—in one of the preparations.

Actinium is always found in uranium minerals, but not in the purely thorium

minerals. B. B. Boltwood found that the ratio U : Ac is fairly constant. Actinium is usually extracted from the residues obtained in the treatment of uranium ores—pitchblende and carnotite. A. Debierne and M. S. Curie obtained the hydroxides of actinium with iron and the rare earths by working up the residues from the pitchblende. The acid soln. was treated with hydrogen sulphide to remove the polonium and radio-lead oxidized; and then treated with ammonia. The precipitate contains hydroxides of actinium mixed with those of iron and the rare earths.

The precipitation by ammonia was found by M. Levin, O. Hahn, B. B. Boltwood, and C. A. von Welsbach to be incomplete in the presence of ammonium salts, and these can be removed by evaporating the soln. to dryness, and heating the residue with boiling nitric acid or aqua regia. The excess of acid is removed by evaporation. H. M. Plum found it impossible to separate all the actinium from radiferous and actiniferous barium chloride in one precipitation even in the presence of aluminium chloride. It required three re-solutions and precipitations to separate the radium and actinium. C. A. von Welsbach noted that actinium is readily separated with manganese when that element is precipitated from basic soln. as manganite. Actinium, unlike thorium and ionium, is not precipitated from its nitrate soln. by the addition of hydrogen peroxide.

The hydroxides are treated with dil. hydrofluoric acid, part—zirconium, titanium, etc.—goes into soln., but most of the radioactive constituent remains with the insoluble fluorides of thorium, cerium, didymium, and lanthanum. The fluorides are then converted into sulphates, then to chlorides, and the soln. treated with oxalic acid, or ammonium oxalate. The conc. of free acid in the soln. for the oxalate precipitation should be reduced to a minimum, since actinium oxalate, like lanthanum oxalate, is distinctly soluble in mineral acids. The precipitated oxalates are then ignited and dissolved in nitric acid. Actinium can be conc. to some extent by fractional crystallization of the double salts with magnesium nitrate or manganese nitrate. The actinium collects with the samarium and neodymium as in the process of E. Demarçay; and it can also be conc. to some extent by taking advantage of the fact that when barium is precipitated as sulphate from a soln. containing barium and actinium, the latter is adsorbed by the precipitate. This property was utilized in the separation of actinium from pitchblende and the ore from Olary (South Australia).

F. Giesel separated the rare earth precipitate by the potassium sulphate and oxalate method, and found the radioactive constituent followed the cerium earths. The actinium was retained very tenaciously by the lanthanum, but it is possible to separate some lanthanum from actinium by the magnesium nitrate process. B. Keetman found that in recrystallizing cerium oxalate from nitric or hydrochloric acid, actinium collects in the most soluble fraction. K. A. Hofmann and F. Zerban employed a process somewhat similar to that used by A. Debierne. They state that actinium oxalate is soluble in a warm soln. of ammonium oxalate, but unlike thorium oxalate, it cannot be reprecipitated by the addition of ammonia or acids; the dried sulphate is only sparingly soluble in ice-cold water; the ignited oxide dissolves readily in conc. sulphuric acid; and it is precipitated by sodium thiosulphate. C. A. von Welsbach found that whereas the contained ionium followed all the reactions of thorium, actinium stands between lanthanum and calcium, but it follows all the reactions of the former. He separated impure actinium from the hydroxide precipitate by what he called the oxalate method and also by the sulphate method.

In the sulphate method, the moist hydroxides were treated with sulphuric acid, and the soln. filtered from the residual basic bismuth sulphate, and the lead and rare earth sulphates. The mother liquid was conc. to remove iron-alum, and treated with oxalic acid. The radioactive actinium in the precipitate followed the reactions of lanthanum. It separated out in several cases as a manganate when the mother liquor from the oxalate precipitations was kept, a reaction which proved of great service, for actinium is, in the presence of ammonium salts, not completely precipitated either by ammonia or ammonium oxalate. From the soln. of the first precipitate of rare earth oxalates, freed from heavy metals, hydroxides were fractionally precipitated in presence of much ammonium nitrate by precipitating a portion with ammonia and stirring it into the main quantity of the

mixture of hydroxides. The most basic part is iron, then come thorium, uranium, scandium, the ytterbium group, the yttrium group, the cerium group, whilst calcium and analogous elements remain in soln. From the rare earths the greater part was removed inactive by precipitation of the sulphates with ammonium sulphate, the radioactive matter keeping with the rare earths in soln., and with those the oxalates of which are soluble in ammonium oxalate (*e.g.* thorium).

In the oxalate method the hydroxides were dissolved in hydrochloric acid, the bismuth precipitated as basic chloride by ammonia, and the filtrate precipitated with oxalic acid and then with ammonia, so long as the oxalate precipitate increased. The soln. of the rare earth oxalates, freed from heavy metals, was precipitated by ammonia as just described so as to give the iron, thorium, and uranium in one fraction, which contained all the radioactive matter. The actinium can be obtained with the lanthanum and the ionium with the thorium by various methods.

There are two descendants of actinium, namely, radioactinium and actinium-X, which, according to O. Hahn and M. Rotenbach, can be separated by the following process. A trace of purified thorium nitrate and a little zirconium nitrate are added, and the radioactinium is separated by treatment with sodium thiosulphate since actinium is not precipitated from a boiling soln. in the presence of that salt; while radioactinium is precipitated by ammonia. A little barium nitrate is added to the soln. to retain the actinium-X, and the actinium is then precipitated with ammonia. The precipitate is dissolved in dil. hydrochloric acid, mixed with barium chloride and sodium acetate, and treated with potassium dichromate, actinium-X separates with the barium chromate. Ammonia precipitates actinium from the filtrate; this is redissolved and reprecipitated a number of times. The operations here indicated should be conducted without delay in order to avoid the re-formation of radioactinium.

According to E. Rutherford, "less is known about actinium as a radioactive element than of any other, for it has been found impossible to isolate it from the rare earths with which it is mixed, and to locate its position in the scheme of transformations." It has not been obtained of a sufficient degree of purity to furnish a characteristic spectrum. The absence of any new lines in the spectrum led E. Rutherford to say that it appears probable that actinium, if it could be obtained in the pure state, would show an activity as great if not greater than that of radium. The preparations of actinium are usually mixtures of compounds of the rare earth elements with very minute proportions of actinium compounds. A. Debierne noted the resemblance which actinium bears to the rare earth elements, and, as F. Giesel, and D. Strömholm and T. Svedberg showed, actinium most resembles the tervalent elements of the cerium group, and more particularly lanthanum, with which it forms isomorphous salts.

For its at. wt., *vide infra*, K. A. Hofmann and F. Zerban estimated the equivalent to be 63·32, but this number is probably too small. G. von Hevesy's diffusion experiments make actinium a tervalent element; and it is isotopic with mesothorium-II. He also found that the presence of actinium in uranium can be shown directly by the emission of its short-lived emanation, when a rapid current of air is aspirated through a soln. of the mineral into an electroscope. D. Strömholm and T. Svedberg found that actinium is not volatile at a red heat under ordinary conditions. Actinium is an unstable element, for, like radium, thorium and uranium, it is continuously breaking down at a slow and definite rate to furnish a consecutive series of disintegration products. Actinium is in a state of equilibrium with these products in about three months after the preparation has been made. In that state, α-, β-, and γ-rays are emitted by actinium preparations; but when freed from these products, actinium is either rayless or emits radiations of very feeble intensity. F. Giesel observed that aged preparations of actinium emit an emanation or a gas whose radioactivity decreases to its half-period value in a few seconds. E. Rutherford illustrates the emanating property of aged actinium by the following experiment:

A highly active preparation of actinium enclosed in thin tissue paper is placed on a screen of phosphorescent zinc sulphide. In a dark room a brilliant phosphorescence, marked

by characteristic scintillations, extends for some distance from the active preparation. On directing a slight current of air across the screen, the phosphorescence is displaced in the direction of the air current, and becomes much feebler. A large part of the phosphorescence observed initially was due to the actinium emanation which diffused through thin paper over the surface of the screen. When the air current ceases, the emanation which is constantly supplied by the actinium, rapidly diffuses over the screen and lights it up again brightly.

The β-rays emitted by actinium in equilibrium with its decay products are of low penetrative power; while the γ-rays are feeble both in intensity and in penetrating power. M. S. Curie estimated the average-life period of actinium to be about 30 years; the estimate was based on the 10 per cent. decrease in the β-ray activity which occurs in old actinium preparation in three years. This estimate was confirmed for an actinium preparation studied for seven years by O. Hahn and L. Meitner, as well as for some recently prepared specimens. From the increase in the α-radiation of the parent of actinium, namely, protoactinium, they estimate a half-life period of 20 years ($\pm$10 per cent.), and an average-life period of 28·8 years. Aged actinium preparations give off α-rays which merge into helium, and, as A. Debierne has shown, they slowly decompose aq. soln. with the evolution of hydrogen and oxygen. S. Meyer estimated the half-life period of actinium to be 16·5 years; and the transformation ratio of actinium and radium in the uranium family to be 4 : 96—E. Rutherford gave 8 : 92; G. Kirsch, 4·2 : 95·8; and O. Hahn and L. Meitner, 3 : 97.

B. B. Boltwood [2] showed that in aged uranium minerals the ratio of the proportion of uranium and actinium is approximately constant. This observation was confirmed by S. Meyer and V. F. Hess, and H. N. McCoy and co-workers. This fact is taken to indicate that actinium is derived from uranium. Since the α-ray activity of actinium is very small in comparison with that of the uranium-radium series of products, in the same mineral, E. Rutherford suggested that some member of the series disintegrates concurrently in two ways, and each of the products continues disintegrating. As a result, there are two series of decay products, one furnishing the actinium and the other the radium series. There has therefore been some speculation as to the precise point at which this branching occurs. It was argued by F. Soddy, from the displacement rule—*vide supra*—that since actinium is a member of the third group of the periodic table, its parent must belong to the fifth group and be a homologue of tantalum if it is formed by an α-ray change; and if formed by a β-ray change, its parent will be a member of the second group isotopic with radium. Radium is the only member of the uranium series in the second group. F. Soddy showed it to be very unlikely that radium is the parent. No actinium was found in a preparation containing 13·2 mgrms. of elemental radium 10 years old. The negative result corresponded with a period of at least 15×10^6 years, whereas the period is shown to be about 30 years. The alternative assumption is that actinium is derived from an element in the fifth group by an α-ray change; and since brevium is short-lived and gives no α-rays, it follows that an unknown isotope must exist in the uranium series. O. Hahn and L. Meitner suggest that the series may branch at uranium-X_1, and β-rays expelled from each so as to furnish two isotopic products. Uranium-Y gives a β-radiation, and therefore its unknown product must occupy the place of ekatantalum in the periodic table, and be isotopic with uranium-X_2 or brevium. If uranium-Y undergoes an α-ray change, the product must be actinium or an isotope, and it should be present in uranium minerals. This was established by F. Soddy and J. A. Cranston. They found uncertain indications of actinium in four-year-old preparations of uranyl nitrate, but increased amounts in preparations eight years old.

O. Hahn and L. Meitner separated the putative parent of actinium, which they called **protoactinium,** from the siliceous residues remaining after the prolonged and repeated treatment of pitchblende with nitric acid so as to remove radium and other radioactive constituents. A little tantalum salt was added, and it was found that the reactions so closely followed those of tantalum that the two elements were

associated together at the end of the operations as inseparable companions. The process employed for the separation of the tantalum and hence also of the protoactinium, was as follows :

A little tantalum oxide was added, and the material extracted with hydrofluoric and sulphuric acids. The addition of a few milligrams of thorium and lead nitrates at this stage serves to keep traces of ionium, uranium-X, and radio-lead in the insoluble form. The filtrate was evaporated to dryness, so as to leave the tantalum and protoactinium in an insoluble form, from which impurities, such as iron, zirconia, and the like, may be removed by boiling with aqua regia. So far, all attempts to separate protoactinium from tantalum have failed. By various elaborations of this method, the whole of the protoactinium from pitchblende containing a known amount of uranium was carefully separated, and its α-activity measured.

The preparation of protoactinium furnished an α-radiation which increased with lapse of time. It was assumed and proved that the α-rays of low range initially produced were derived from protoactinium, while the α-rays of longer range were due to the growth of actinium and its decay products. The range of the α-rays of protoactinium in air at 0° and 760 mm. was 3·314 cms. Actinium does not follow H. Geiger and J. M. Nuttall's relation so closely as other radioactive series, and there is a considerable difference in the constants according as actinium-X or radioactinium is taken for the comparison—the former furnishes 1700 years and the latter 260,000 years in the period of average life of protoactinium. The at. wt. and spectrum have not been determined, but all the evidence shows that protoactinium is the ekatantalum of the periodic table or an isotope of that element. If the life period of protoactinium is 1200 years, for each gram of radium in uranium minerals there should be 60 mgrms. of protoactinium ; and if the life period is 180,000 years, 9 mgrms.

The putative parent of protoactinium is uranium-Y. As previously indicated, it is not clear if uranium-Y is derived from uranium-I or uranium-II—if the former, the at. wt. of protoactinium will be 234, and of actinium 230 ; while if uranium-Y is derived from uranium-II, as K. Fajans believes is more probably the case, the at. wt. of protoactinium will be 230, and that of actinium 226. According to these hypotheses, the uranium series furnishes :

$$U \rightarrow U_I \rightarrow U_{X_1} \rightarrow U_{X_2} \rightarrow U_{II} \begin{cases} \rightarrow Io \rightarrow Ra \rightarrow RaEm \rightarrow \\ \rightarrow U_Y \rightarrow Pa \rightarrow Ac \rightarrow \end{cases}$$

A. Piccard suggested that actinium is possibly derived from a third isotope of uranium of at. wt. 239, which does not belong to the uranium family at all, but is a distinct primary radio-element, like uranium or thorium. He suggested the name *actino-uranium*, Act_U, for this hypothetical element. He supported this view by assuming that O. Hönigschmid's value 239·16 for the at. wt. of uranium indicates that the assumed uranium is really a mixture of 92 per cent. of an isotope of at. wt. 238 which belongs to the radium series, and 8 per cent. of one with an at. wt. 240 which would make the at. wt. of protoactinium 236, and that of actinium 232. H. Geiger and J. M. Nuttall's curves also show that the three series are not superposed, but furnish parallel lines indicating that each of the three is an independent primary series. The constants are the same for each series, but different for different series. F. Soddy objects that the ratio of actinium to radium in uranium minerals is nearly constant, and this would mean the accepting of the unlikely chance that actinouranium has the same period as uranium-I. These possibilities can be settled when the at. wt. of actinium or protoactinium has been determined. A. Piccard's hypothesis is supported by E. Q. Adams. E. Marsden and A. B. Wood's diffusion experiments showed that the at. wt. of actinium emanation is 232 ; this would make the at. wt. of actinium itself 240—rather greater than uranium—on the assumption that 8 units are to be added for the α-particles of radioactinium and actinium-X. A. Smekal discussed the atomic structure of the parents of radioactinium.

In his investigation on the relation between the actinium and uranium series, O. Hahn[3] encountered a new radioactive substance which is separated with proto-actinium, and the two radioactive substances are isotopic. The isotope of proto-actinium was provisionally called **uranium-Z,** U_Z. It has a half-life period of 6·7 hrs. and gives off complex α-rays which are half absorbed by layers of aluminium 0·014 to 0·12 mm. thick. Only small proportions are present, and the intensity of its radiations is about 0·25 per cent. of that of U_X, that is, $U_X + U_{X^2}$. Assuming that uranium-Z is not derived from uranium-X, whereby both pass into uranium-II by the loss of β-rays, it is suggested that there is possibly a new uranium-III series analogous with the uranium-I series, just described. The hypothetical uranium-III is said to be analogous with uranium-I, and to have an at. mass of 240; and it furnishes uranium-Z_1 and uranium-Z_2 analogous with uranium-X_1 and uranium-X_2 respectively: $\underset{240}{U_{III}} \rightarrow \underset{236}{U_{Z_1}} \rightarrow \underset{236}{U_{Z_2}} \rightarrow \underset{236}{U_{IV}} \rightarrow ?$ It is considered to be improbable that uranium-I represents the mother substance of uranium-Z, and that the latter is derived from the former by the loss of a particle of mass 3. M. C. Neuburger suggests the alternative schemes:

$$U_I \begin{cases} \rightarrow U_{X_1} \rightarrow U_{X_2} \rightarrow U_{II} \rightarrow \ldots \\ \rightarrow U_{Z_1} \rightarrow U_{Z_2} \rightarrow U_{III} \rightarrow \ldots \end{cases}; \quad U_I \begin{cases} \rightarrow U_{X_1} \rightarrow U_{X_2} \\ \rightarrow U_{Z_1} \rightarrow U_{Z_2} \end{cases} \begin{matrix} \rightarrow U_{II} \\ \rightarrow \end{matrix} \begin{cases} \rightarrow Io \rightarrow \ldots \\ \rightarrow U_Y \rightarrow \ldots \end{cases}$$

but prefers the latter. The subject has also been discussed by A. Smekal, and O. Hahn; the latter said that the suggestion of M. C. Neuburger is improbable and lacks experimental foundation.

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§ 13. The Decay Products of Actinium

While studying the radioactivity of a preparation of actinium freed from actinium-X, O. Hahn [1] found that the activity increased to a maximum much more slowly than would be expected if actinium were transformed directly into actinium-X. He showed that not actinium but another product, which he called **radioactinium,** RaAc, is the direct parent of actinium-X; and that the first product of the decay of actinium is probably radioactinium. This product concentrates in the first fractions when a soln. of an actinium salt is fractionally precipitated with ammonia; and by successive precipitations it is possible to obtain radioactinium almost free from actinium and actinium-X. Radioactinium is also precipitated with sulphur when a soln. is boiled with an excess of sodium thiosulphate. The sulphur is expelled from the precipitate by heat. F. Giesel, M. Levin, and A. Fleck obtained it by adding a little thorium salt to an acid soln. of a preparation of actinium, and boiling with an excess of sodium thiosulphate; the precipitated basic thorium thiosulphate carries down some radioactinium. O. Hahn and M. Rotenbach used a zirconium salt in place of the thorium salt—*vide* purification of actinium. The latter is also deposited on charcoal when the soln. is shaken therewith. H. N. McCoy and E. D. Leman prepared radioactinium, by adding a trace of a thorium salt to the soln., and precipitating the latter by hydrogen peroxide at 60°. A. Fleck discussed the isotopy of uranium-X, thorium, and radioactinium.

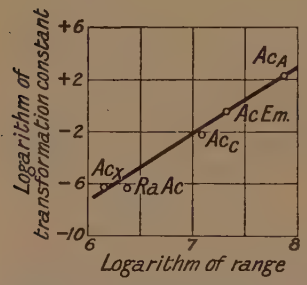
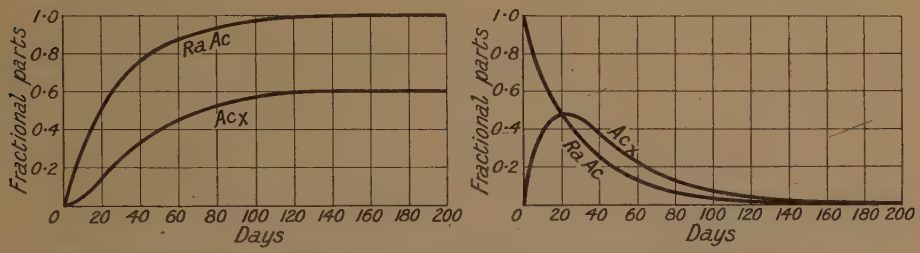


Fig. 16.—H. Geiger and J. M. Nuttall's relation between the Range of the α-rays and the Period of Transformation.

A. S. Russell and J. Chadwick thought that they had resolved radioactinium into two components, radioactinium-I with a half-life period of 19·5 days and radioactinium-II with a half-life period of 13 hrs.; but O. Hahn and L. Meitner could not establish this hypothesis, and they believed that the alleged radioactinium-II is really thorium-B, which has a half-life period of 10·6 hrs., and might easily be present in the products.

Radioactinium is not appreciably volatile at a red heat under ordinary experimental conditions. It emits α-, β-, and γ-rays. The α-rays were found by H. Geiger and J. M. Nuttall to have a range of 4·36 cms.; H. N. McCoy and E. D. Leman, 4·17 cms.; and S. Meyer, V. F. Hess, and F. Paneth, 4·2 cms. to 4·60 cms. in air at 15° and normal press. In general, the range of the α-particles in air is directly proportional to the absolute temp., and inversely proportional to the press. E. Rutherford found the velocity to be $1{\cdot}68\times10^9$ cms. per sec. O. von Baeyer, O. Hahn and L. Meitner found the magnetic spectrum of the β-rays showed rays with a velocity, V, of $1{\cdot}14\times10^{10}$, $1{\cdot}26\times10^{10}$, $1{\cdot}47\times10^{10}$, and $1{\cdot}59\times10^{10}$ cms. per sec., or the velocity is equal to the fractional part, V/V_∞ 0·38, 0·42, 0·49, 0·53 of the velocity of light, V_∞. The coeff. of absorption of the β-rays in aluminium is 175 cms. The absorption coeff. of the γ-rays is 25 and 0·19 cm.$^{-1}$ of aluminium. The product of the decay of radioactinium is actinium-X. The rate of formation of radioactinium from actinium is shown in Fig. 17, calculated from $\text{RaAc}=1-e^{-\lambda_1 t}$, where $\lambda_1=0{\cdot}0356$ day, when $t=0$, Ac-X=0, and RaAc=1·00. The rate of decay of radioactinium is shown in Fig. 18, calculated from $\text{RaAc}=e^{-\lambda_1 t}$. According to H. N. McCoy and E. D. Leman, the half-life period of radioactinium is 18·88 days or $4{\cdot}1\times10^7$ secs.; O. Hahn gave 19·5 days or $4{\cdot}25\times10^7$ secs. There is a discrepancy between the life period calculated by H. Geiger and J. M. Nuttall's equation. This is taken

to indicate that radioactinium is not homogeneous, and, by analogy with thorium, it is possible that a meso-product is present. The average-life period is 21·8 days to 27·24 days. The radioactive constant $\lambda=4{\cdot}25\times10^{-7}$ secs. or $\lambda=4{\cdot}10\times10^{-7}$ secs. or 0·0356 day.



FIGS. 17 and 18.—Formation and Decay Curves of Radioactinium and Actinium-X.

About the same time, F. Giesel,[2] and T. Godlewsky separated a product, called **actinium-X,** AcX, from actinium preparations by the precipitation of the actinium with ammonia, the actinium-X remains in soln. It was at first regarded as the decay product of actinium, and by analogy with the radioactinium substance first derived from uranium, it was called actinium-X. Actinium-X is derived from preparations of actinium which have stood many months in a closed vessel so that it is in equilibrium with its decay products. F. Giesel, S. Meyer and E. von Schweidler, and O. Hahn obtained it by recoil from radioactinium on a negatively charged plate. T. Godlewsky obtained it by precipitating actinium and radioactinium from a preparation of actinium by ammonia, the actinium-X remains in the filtrate. To ensure the efficacy of the process, O. Hahn and M. Rotenbach allowed the filtrate to stand two hours on a water-bath, acidified the soln., and re-precipitated by adding a little ferric salt and then ammonia. A. Debierne found that when barium is precipitated as sulphate in a soln. containing actinium, a radioactive substance is co-precipitated which decays with time. This is now thought to have been actinium-X. H. N. McCoy and E. D. Leman recommended adding a little barium salt to the filtrate, and removing the actinium-X from the soln. by co-precipitation with barium sulphate ; or else evaporating the filtrate to dryness, and heating the residue to expel the other decay products, since actinium-X is not volatile at a red heat. H. N. McCoy and E. D. Leman also separated actinium-X by adding a little thorium salt to the soln., and precipitating the thorium with hydrogen peroxide. The precipitation was repeated a number of times, actinium-X and thorium-X remain in the soln. If an ammoniacal soln. of an actinium preparation is electrolyzed, actinium-X, actinium-A, and actinium-B are deposited on the cathode.

Actinium-X behaves like radium in many reactions, and D. Strömholm and T. Svedberg emphasized the analogies between actinium-X and thorium-X. They are indistinguishable as regards chemical properties, and probably both belong to the group of alkaline earths. G. von Hevesy's diffusion experiments show actinium-X to be bivalent. Actinium-X nitrate crystallizes isomorphously with barium nitrate. It is not volatile at a red heat. Its parent is radioactinium and its decay product is actinium emanation. The rate of formation of actinium-X from radioactinium is shown in Fig. 17, calculated from

$$\mathrm{Ac_X}=0{\cdot}596\left(1+\frac{\lambda_1}{\lambda_2-\lambda_1}e^{-\lambda_2 t}-\frac{\lambda_2}{\lambda_2-\lambda_1}e^{-\lambda_1 t}\right)$$

where the constants are $\lambda_1=0{\cdot}0356$ day and $\lambda_2=0{\cdot}0597$ day, and at $t=0$, RaAc $=1{\cdot}00$, and AcX$=0$. The rate of decay of actinium-X is shown in Fig. 18, calculated from

$$\mathrm{Ac_X}=\frac{1}{\lambda_2-\lambda_1}(e^{-\lambda_1 t}-e^{-\lambda_2 t})$$

At the time t=21·44 days, the number of atoms of actinium-X present is a maximum. H. Geiger and J. M. Nuttall found that the α-rays emitted by actinium-X have a range 4·40 at 15° and 760 mm. press., and the initial velocity computed by E. Rutherford is $1{\cdot}65\times10^9$ cms. per sec.; S. Meyer, V. F. Hess and F. Paneth observed the range 4·26 cms. and initial velocity $1{\cdot}63\times10^9$ cms. at 15°. For the half-life period, S. Meyer and E. von Schweidler obtained 11·8 days; O. Hahn and M. Rotenbach, 11·6 days; and H. N. McCoy and E. D. Leman, 11·2 days; the average-life period is 16·45–16·7 days; and the decomposition constant $\lambda=7{\cdot}04\times10^{-7}$ secs. or 0·0597 day.

F. Giesel [3] discovered in 1902 that actinium preparations gave off an emanation which was also studied by A. Debierne. Actinium emanation, AcEm, is an inert gas which changes very rapidly—*vide supra*, the proportions of actinium. On account of its short life, the gas has not been isolated in a pure state. It can be removed from actinium soln. by the passage of a rapid stream of air or other gas; it is also readily evolved from most solid preparations of actinium—particularly actinium-lanthanum oxide, hydroxide, oxalate, nitrate, manganite, fluorosilicate, sulphate, etc. Raising the temp. also favours the evolution of the gas. H. Herschfinkel has made observations on this subject.

F. Giesel showed that actinium emanation behaves like a gas. It excites the phosphorescence of barium cyanoplatinate and zinc sulphide. A. Debierne measured the half-life period of decay of actinium emanation and found it to be 3·9 secs.; and O. Hahn and O. Sackur obtained a similar result, and showed that the periods from F. Giesel's emanation, and A. Debierne's actinium were identical. The actinium emanation has virtually disappeared in one minute. S. Kinoshita, and P. B. Perkins, found the half-life period to be 3·92 secs., and M. S. Leslie, 3·91. This gives for the average-life period, 5·55 secs.; and for the radioactive constant, 0·18 sec. F. Giesel said that the emanation is positively charged, but in view of the short period of decay, it is possible that the effect was produced by some of the products of decay. From the effects on the ionization of gases, H. L. Bronson inferred that the emanation in decomposing gives off two α-particles for each α-particle given off by the active deposit in equilibrium with the emanation. This was confirmed by H. Geiger and E. Marsden, and it shows that either the emanation gives off two α-particles or there must be an intermediate α-ray radiating product. H. Geiger showed that the last hypothesis is correct, and the half-life period of this intermediate product is 0·002 sec. The decay of actinium emanation is attended by the emission of α-particles which, as A. Debierne, and F. Giesel showed, furnish helium gas. The range, R, of the α-particles in air at 15° was found by O. Hahn to be 5·8 cms.; S. Meyer, V. F. Hess, and F. Paneth, 5·57 cms.; and H. Geiger, 5·7 cms.; at 0°, H. Geiger and J. M. Nuttall found 5·4 cms. The initial velocity, V, of the α-rays, calculated from $V^3=1{\cdot}33\times10^{27}R$, is $1{\cdot}93\times10^9$ cms. per sec. S. Meyer and co-workers found $1{\cdot}78\times10^9$ cms. per sec. H. Geiger and J. M. Nuttall's relation between the radioactive constant, λ, and the range, R, is shown in Fig. 11. H. A. Wilson's relation $\log\lambda-\log R=a+bR^{-\frac{3}{2}}$, where a and b are constants; and R. Swinne's relation $\log\lambda=a+bV$, where a and b are constants, are also in agreement with observations on actinium emanation. The kinetic energy of the α-rays is $1{\cdot}15\times10^{-5}$ ergs.

W. Ramsay, and O. Hahn said that emanation rises in air as if it were specifically lighter than that menstruum, but this may be due to its having been explosively ejected from the solid, or to the emanation being hotter than the ambient air. A. Debierne measured the coeff. of diffusion, K, of actinium emanation, and found 0·112; for carbon dioxide, the coeff. was 0·142; hence, from Graham's diffusion law, the mol. wt. of radium emanation is about 70. This number is very improbable. S. Russ observed for the coeff. of diffusion in air, 0·096–0·122; in hydrogen, 0·330; in carbon dioxide, 0·073; in sulphur dioxide, 0·062; in argon, 0·106–0·109. For the effect of press. p mm., on the coeff. of diffusion, K, he found:

p	14	41	80	155	371	558	764
K	7·81	2·37	1·16	0·582	0·248	0·167	0·125
pK	109	97	93	90	92	93	95

and from a comparison of the coeffs. of diffusion, he found the mol. wt. of thorium emanation to be 1·42 times that of actinium emanation. G. Bruhat found that the effect of temp. and press. of the coeff. is such that pK/T^2=a constant:

p mm. . .	760	367	209	127	97	52	36	25	9
θ . . .	15	15	13·5	16·3	14·8	15	16	13	12·3
K . . .	0·112	0·245	0·404	0·55	0·93	1·62	2·29	3·65	9·1
$(pK/T^2)\times10^3$.	10·2	10·3	10·2	8·5	10·8	10	10	11	10

The average of the constant is 0·00101; and therefore for p=760, and θ=15°, K=0·113. The mean value of S. Russ is 0·115 between 10° and 18°; hence, all three workers obtained approximately the same value for the diffusion coeff. of actinium emanation in air. For the ratio K_{CO_2}/K_{air}, G. Bruhat found 0·68, and S. Russ, 0·76; for K_{H_2}/K_{air}, G. Bruhat gave 3·65, and S. Russ, 3·44. For other materials, G. Bruhat found for ratios of the diffusion constants of the following vapours in the gases named:

	Ether.	Methyl alcohol.	Ethyl alcohol.	Formic acid.	Acetic acid.	Ethyl formate.	Benzene.	Water vapour.	Carbon dioxide.
CO_2/Air .	0·71	0·66	0·67	0·67	0·67	0·67	0·70	0·67	—
H_2/Air .	3·8	3·8	3·7	3·9	3·8	3·9	3·5	3·5	3·8

For actinium emanation, the values are 0·68 and 3·7 respectively, thus showing that the emanation behaves like an ordinary gas. M. S. Leslie also determined values of p and K, and obtained 0·098 for the value of K at 15° and 760 mm. The result is dependent to some extent on the form of the apparatus. With thorium emanation, the corresponding value was 0·085. Hence, the mol. wt. of the two emanations are not very different. The mol. wt. calculated from the diffusion coeff. are too small in the case of radium, thorium, and actinium emanations. It has not yet been proved that Graham's law of gaseous diffusion is applicable to the case of an exceedingly small proportion of a radioactive gas diffusing into an enormous proportion of another gas. K. Fajans concluded that radium and actinium emanations have the same at. wt. E. Marsden and A. B. Wood obtained the mean value 232 for the at. wt. of actinium emanation, from diffusion in vacuo.

E. Goldstein observed the condensation of actinium emanation at the temp. of liquid air, and E. Henriot found that at —143°, the vap. press. is imperceptible. S. Kinoshita found that condensation begins at —120°, and is complete at —150°. E. Goldstein found the b.p. to be —65°. G. von Hevesy measured the solubility of actinium emanation in different liquids, and found the order with increasing solubility to be the same as for niton. Hence, he concluded that actinium emanation belongs to the same group of inert gases as niton. If the solubility of actinium emanation in water is unity, that in a sat. soln. of potassium chloride is 0·9, in conc. sulphuric acid, 0·95; and in

Ethyl alcohol.	Amyl alcohol.	Benz-aldehyde.	Benzene.	Toluene.	Petroleum.	Carbon disulphide.
1·1	1·6	1·7	1·8	1·8	1·9	2·1

The partition coeff. between water and air is about 2; with thorium and radium emanations, the values are respectively 1·0 and 1·3. F. Giesel found that thin celluloid arrests the emanation. According to G. von Hevesy, wood charcoal absorbs the emanation greedily; at 18° the partition coeff. between carbon and the gas phase (with hydrogen is above 20), and he gave the following comparison:

Helium.	Argon.	Actinium em.	Thorium em.	Radium em.
2	12	20	50	100

The parent of actinium emanation is actinium-X, and its immediate successor is actinium-A, which in turn passes into actinium-B, actinium-C and -C′, and actinium-D. As in the case of radium, actinium can under certain conditions impart a temporary radioactivity to bodies in its neighbourhood. A substance exposed for some time in the presence of actinium behaves as if its surface were coated with an invisible film of radioactive matter. This *induced or excited radioactivity* is derived

from the transformation of actinium emanation. The surface of a body exposed to the emanation becomes coated with an invisible film of radioactive matter, called, for convenience, the *active deposit of actinium.* This deposit emits α-, β-, and γ-rays. To obtain the active deposit, a current of air laden with the emanation is passed through a metal cylinder provided with a metal electrode held axially in position, and insulated from the cylinder by rubber-stoppers. If a potential of about 50 volts is maintained between the central negatively charged electrode and the positively charged cylinder, the active deposit collects on the electrode. The distribution of the active deposit on an electric field has been studied by E. M. Wellisch,[4] S. Russ, H. T. Brooks, W. T. Kennedy, J. C. McLennan, and H. P. Walmsley. According to A. N. Lucian, in dust-free dry air, (i) the percentage of actinium active deposit collected on the cathode increases with increasing potential to a definite limit of 95 per cent. as the maximum, the remaining 5 per cent. consisting of neutral particles, arrive at the electrodes by diffusion. (ii) No negative particles take part in the distribution. (iii) For lower values of the cathode deposit, the formation of neutral deposit particles results both by volume recombination and columnar recombination of the positively charged particles with negative ions. Both types of recombination occur at a faster rate for the deposit particles than for ordinary positive ions, due to their larger mass and size and slower speed. In all respects the actinium active deposit behaves, qualitatively at least, like that of radium. It is supposed that the recoiling deposit particle, in its collision with the molecules in its path, expels from them negative electrons with much greater velocity than is imparted to the positive ion, so that the recoil particle is surrounded by an overwhelming majority of positive ions, and there is a greater probability that it will emerge positively charged than otherwise. The fact that the limiting value for the cathode deposit is for actinium (95 per cent.) greater than for radium (98 per cent.) is what is to be expected from the fact that the actinium-A atom recoils with a greater velocity than the radium-A atom.

As previously indicated H. L. Bronson found that twice as many α-particles were expelled from actinium emanation as were expelled by actinium-C in equilibrium therewith. H. Geiger and E. Marsden noted that the α-particles from actinium emanation appeared as doubles, indicating either that the atom in breaking up emits two α-particles, or that the emanation gives rise to another α-ray product which is very rapidly transformed. The latter hypothesis was established. The two α-particles follow one another with less than $\frac{1}{10}$th sec. interval. The manner in which the α-ray activity of the active deposit varies with time depends on how long is taken to collect it; if under 10 secs., the activity increases slightly with time, reaches a maximum in 7 mins., and then decreases according to an exponential law; while if over 10 secs., H. T. Brooks observed no initial rise in the α-ray activity. The first transient product of the decay of actinium emanation is a solid, but with a very short life, so that it is usually associated with the emanation. It is called **actinium-A,** AcA. The very short life of actinium-A does not allow it to be isolated and studied in the ordinary way. H. G. J. Moseley and K. Fajans deposited the active matter from actinium emanation on the face of a negatively charged rapidly rotating disc; the radioactivity of the deposit was examined at different angular distances by electrical methods. It was thus found that actinium-A emits α-rays, and that its half-period is 0·002 sec. Actinium-A has the shortest life of any of the radioactive elements yet observed. According to S. Meyer and co-workers, the range of the α-particles in air at 15° is 6·27 cms.; while, according to H. Geiger and J. M. Nuttall, the range is 6·5 cms. at 15°. The average-life period is 3×10^{-3} secs., and the radioactive constant $\lambda=346$ secs.

L. Meitner found that if an acid soln. of the active deposit of actinium is electrolyzed with silver electrodes, actinium-B, and -C with an excess of actinium-A, is deposited on the cathode. It is thought that actinium-A is chemically analogous with radium-A and thorium-A, and isotopic with polonium. Its nearest companion in the periodic table is tellurium.

Actinium-A is very rapidly changed into **actinium-B,** AcB. This product was discovered by A. Debierne and called actinium-A; what is at present known as actinium-A was discovered later. The changed notation is due to E. Rutherford and H. Geiger. Actinium-B passes into **actinium-C,** AcC, discovered by E. Rutherford, and H. T. Brooks in 1904. It was first called *actinium-B.* H. T. Brooks found that the activity curves of the active deposit of actinium depended greatly on the time of exposure. The activity at first increases, passes through a maximum, and decreases according to an exponential law with a period of 36 mins. H. L. Bronson measured the activity curve for short exposures. This is shown in Fig. 19, where the maximum activity is taken at 100. E. Rutherford showed that the curve is characteristic of one involving two products, one emitting α-rays, the other no α-rays. The decrease in activity fixes the period of one of these products at 36 mins. and $\lambda=0{\cdot}0192$ min. H. L. Bronson found that $\lambda_2=0{\cdot}322$ min. for the other, or the period of the second product is 2·15 mins. H. T. Brooks showed that in the electrolysis of the active deposit of actinium, an α-ray product was obtained with a half-life period of 1·5 min. S. Meyer and E. von Schweidler showed that when a platinum plate is coated with the active deposit and heated to a bright red heat, the residual matter emits α-rays and decays with a half-life period of 1·5 min. O. Hahn and L. Meitner further showed that the residual α-ray product had a half-life period of 2·15 mins. Hence, the product with a half-life period of 36 mins., with no α-rays, is actinium-B, and it volatilizes at a high temp., while the α-ray product, which does not volatilize, is actinium-C. M. Levin showed that actinium-B begins to volatilize at 400°, and it is completely volatilized in 10 mins. at 750°, in 4 mins. at 900°, and in about half a minute in a blowpipe flame. Actinium-C is not perceptibly volatilized below 700°. A. Fleck discussed the isotopy of radium-B, and actinium-B; and the possible isotopy of thorium-C, radium-C, and actinium-C.

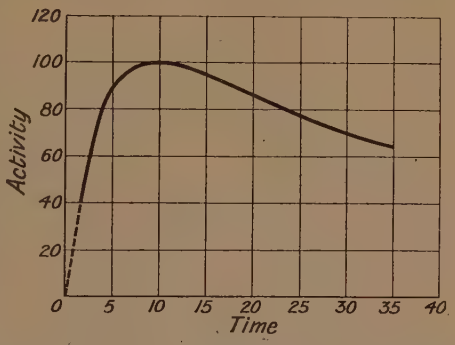


FIG. 19.—Decay Curve of the Active Deposit of Actinium.

A. Debierne first supposed it to be rayless; but O. Hahn and L. Meitner showed that it emits feeble β-rays which have an absorption coeff. in aluminium of 10^3 cms.$^{-1}$, and a velocity of $1{\cdot}80\times10^{10}$ to $1{\cdot}98\times10^{10}$ cms. per sec., or 0·63 when the velocity of light is unity. Actinium-B was also found by E. Rutherford and H. Richardson to emit γ-rays with an absorption coeff. in aluminium of 120, 31, and 45 cms.$^{-1}$. The half-life period of actinium-B by A. Debierne is 40 mins.; by H. T. Brooks, 41 mins.; by J. Elster and H. Geitel, 34·4 mins.; by S. Meyer and E. von Schweidler, 35·8; H. L. Bronson, 35·7; O. Hahn and O. Sackur, 36·4 mins.; by T. Godlewsky, 36 mins.; by V. F. Hess, 36·07 mins.; and by H. N. McCoy and E. D. Leman, 36·2 mins. The mean value is 36 mins.; the average-life period is 52·1 mins.; and the radioactive-constant $\lambda=3{\cdot}20\times10^{-4}$ secs. Actinium-B is isotopic with lead, and its chemical properties resemble those of lead. L. Meitner deposited it electrolytically from soln. of its salts—*vide supra*—and if a nickel plate be dipped in a boiling feeble acid soln. of the active deposit of actinium for one to two minutes, actinium-B is deposited on the metal. After actinium-B has been volatilized in air, H. Schrader found the product to be much less volatile, and it can be condensed on a surface at 1000°; in an atm. of hydrogen, the condensation occurs several degrees lower than in air; this is presumably due to the formation of an oxide. Again, if the active deposit be exposed to bromine vapour, to chlorine, to hydrogen bromide, or to hydrogen iodide for 10–15 mins., the velocity of actinium-B is augmented. The last

two gases cause actinium-C to become more volatile, and after treatment with hydrogen iodide, actinium-C is more volatile than actinium-B. Exposure to hydrogen chloride does not affect the volatility, but if the active deposit which has been exposed to hydrogen chloride be treated with water, nearly all the actinium-B is dissolved, but no actinium-C. Actinium-B is readily dissolved by hydrochloric acid. If the active deposit of actinium be immersed for one minute in 0·001*N*-hydrochloric or sulphuric acid, 80–85 per cent. of the actinium-B is dissolved, and no actinium-C.

E. Rutherford and H. T. Brooks separated actinium-C by the electrolysis of a boiling hydrochloric acid soln. of actinium-B or of actinium-X between platinum electrodes. As indicated above, S. Meyer and E. von Schweidler, and M. Levin found that at about 700°, actinium-B volatilizes from a film of the active deposit of actinium on platinum, leaving actinium-C behind. Actinium-C is said to be isotopic with bismuth. It emits α- and β-rays which, according to H. Geiger and J. M. Nuttall, have a range of 5·40 cms. in air at 15°, and an initial velocity of $1{\cdot}77\times10^9$ cms. per sec. at 0°; S. Meyer and co-workers gave 5·15 cms. for the range in air at 15°, and $1{\cdot}74\times10^9$ cms. per sec. for the initial velocity at 0°. H. T. Brooks, H. L. Bronson, and O. Hahn and L. Meitner found the half-life period to be 2·15 mins.; the average-life period 3·12 mins., and the radioactive constant $\lambda=5{\cdot}33\times10^3$ secs.

From the close analogies between actinium-C, radium-C, and thorium-C, it might be anticipated that actinium-C would show peculiarities in its mode of transformation. L. Blanquies found that the variation of ionization along the path of a pencil of α-rays from actinium-C was rather different from the corresponding curves of polonium, and it appeared that actinium-C is complex, furnishing two α-ray products. E. Marsden and co-workers showed that actinium-C decomposed into two radioelements, one **actinium-D**—also called actinium-C″—an α-ray product, and the other, **actinium-C_2**—also called actinium-C′—a β-ray product. The latter transformation represents about 0·15 or 0·2 per cent. of the whole. Actinium-C_2 gives off α-rays with a range of about 6·4 cms. in air at 15°; its half-life period is about 5×10^{-3} secs., its average-life period is about 7×10^{-3} secs., and its radioactive constant $\lambda=140$ secs. approximately. This product is not very well known. It is assumed to be isotopic with polonium. The changes in the constituents of the active deposit of actinium are therefore summarized:

$$\mathrm{AcA} \xrightarrow{\alpha} \mathrm{AcB} \xrightarrow{\beta} \mathrm{AcC} \begin{cases} \xrightarrow{\alpha} \mathrm{AcD} \rightarrow \\ \xrightarrow{\beta} \mathrm{AcC_2} \rightarrow \end{cases}$$

E. Albrecht obtained for the relation Ac-C_2 : Ac-C=99·84. The β-rays and γ-rays of the active deposit of actinium were initially ascribed to actinium-C, but O. Hahn and L. Meitner showed that these rays are derived from the decay product of actinium-C, namely, actinium-D. While the α-ray activity of actinium-C decays with a half-life period of 2·15 mins., the β-ray activity passes through a maximum in about 5 mins., and then decays exponentially with a half-life period of 5·1 mins., the increase in the β-ray activity is due to the formation of actinium-D. O. Hahn and L. Meitner obtained actinium-D by the method of recoil. A negatively charged plate was brought near another parallel plate coated with the active deposit of actinium; in a few minutes, about 20 per cent. of the total amount of actinium-D formed in the interval of exposure is transferred to the recoil plate. Actinium-D in the form of soot was separated from an acid soln. of the active deposit on spongy platinum or carbon. If a platinum plate covered with a film of the active deposit be exposed for a short time to a high temp., the actinium-B and -D are almost completely volatilized, and the remaining actinium-C decays as indicated above.

O. Hahn and L. Meitner found the half-life period of actinium-D to be 5·1 mins., while A. F. Kovarik obtained 4·71 mins.; the corresponding average-life period, 6·8 mins.; and its radioactive constant $\lambda=2{\cdot}45\times10^{-3}$ secs. T. Godlewsky found the coeff. of absorption for aluminium to be $32{\cdot}7$ cms.$^{-1}$, and O. Hahn and L. Meitner, $28{\cdot}5$ cms.$^{-1}$. O. von Baeyer obtained for the magnetic spectrum of the β-rays of the active deposit of actinium, rays with velocities $1{\cdot}80\times10^{10}$, $1{\cdot}98\times10^{10}$, $2{\cdot}22\times10^{10}$,

and $2{\cdot}73\times10^{10}$ cms. per sec. E. Rutherford and H. Richardson found the absorption coeff. of the γ-rays of actinium-D to be 0·198 cm.[1] of aluminium. Actinium-D is said to behave chemically like thallium, and to be isotopic with thorium-S and radium-C_2.

It has been shown that two different lines of argument on the origin of actinium, furnish the at. wt. 226 if derived from uranium-II, and 230 if derived from uranium-I. The former hypothesis is generally accepted, and allowing a reduction of four units for each α-ray transformation, the at. wt. of the other members of the actinium series are readily estimated. This gives the genealogical tree shown in Table VIII. A summary of the radioactive properties of the members of the series is given in Table IX; and the position of the individual members of the actinium series in the periodic table is given in Fig. 20.

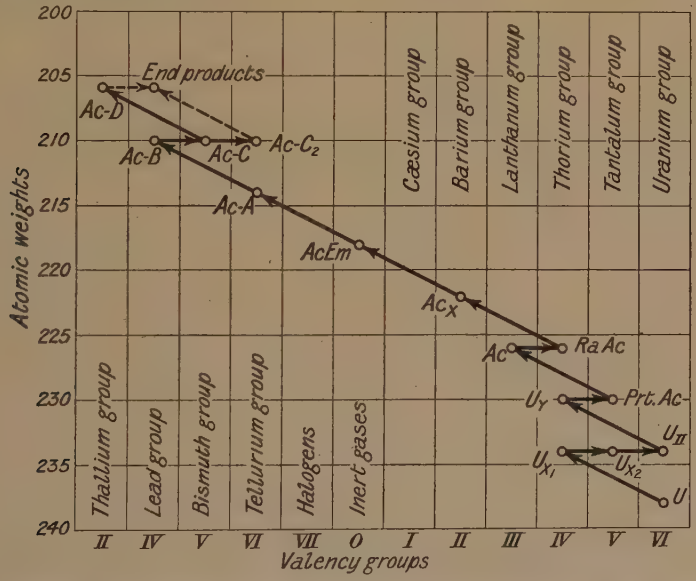


FIG. 20.—Position of the Members of the Uranium-Actinium Series in the Periodic Table.

The nature of the end-product of the decay of actinium-C_2 by the expulsion of an α-particle is unknown; the at. wt. of this product, 210—4=206, makes it appear as if an isotope of lead is produced. Only 2 per cent. of the parent actinium-C is so converted; the remaining 98 per cent. changes into actinium-D, which, on account of the at. wt. 206, appears as if it is an isotope of lead; and since actinium-D gives off β-rays, it passes into actinium-E, AcE, which, having the same at. wt., is possibly another isotope of lead. It was shown in connection with the end-products of radium that the at. wt. of lead extracted from uranium minerals free from thorium is always less than 207·2, the at. wt. of lead derived from non-radioactive sources. The at. wt. of a number of samples of lead from uranium minerals is 206·04, and if approximately 8 per cent. of this is derived from the actinium branch, and the at. wt. of actinium-E is 210·1, instead of 206, the at. wt. of lead should be 206·4. A. Holmes and R. W. Lawson argue that if the at. wt. of actinium-E is 210, it is an unstable element and is disintegrating, while the end-product of the radium series is accumulating. If actinium-E is slowly disintegrating with the emission of β-rays, it would form an isotope of bismuth; and the at. wt. of bismuth extracted from uranium minerals would not be 208, characteristic of bismuth from non-radioactive sources. If actinium bismuth is unstable the loss of an α-particle per atom would convert it into a thallium isotope, but analyses of uranium minerals for thallium are not available to test the suggestion of A. Holmes and R. W. Lawson.

TABLE VIII.—GENEOLOGICAL TREE OF ACTINIUM FAMILY.

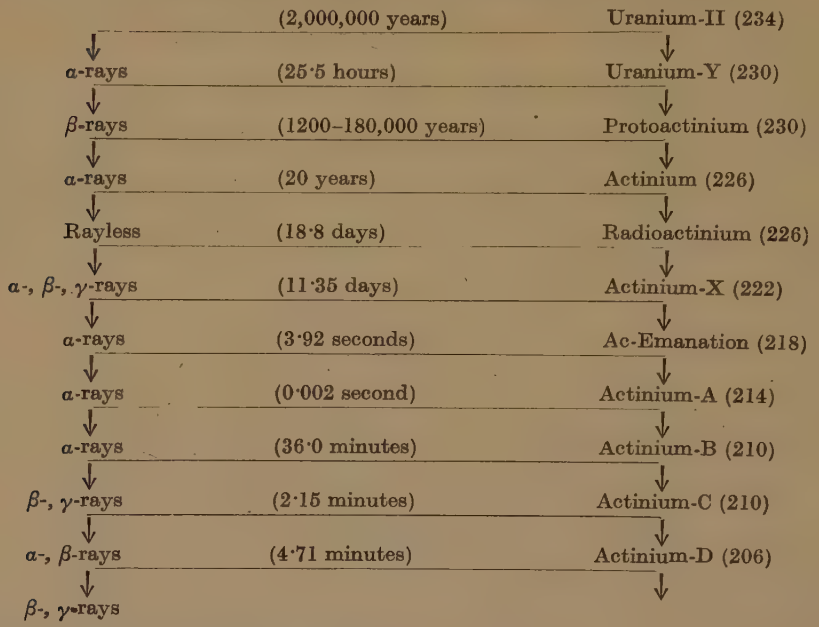


TABLE IX.—PROPERTIES OF THE URANIUM-ACTINIUM FAMILY OF RADIOACTIVE ELEMENTS.

Radioactive element.	Symbol.	Atomic weight.	Half-life period.	Radioactive constant sec.	Radiation.	Range of α-rays cm.	Velocity of α-rays cm. per sec.
Uranium-Y	UrY	230	25·5 hrs.	$7·55 \times 10^{-6}$	β	—	—
Protoactinium.	Pa	230	1700–180,000 yrs.	—	—	3·314	—
Actinium	Ac	226	20 yrs.	—	O	3·56	$1·54 \times 10^{9}$
Radioactinium	RaAc	226	11·88 dys.	$4·25 \times 10^{-7}$	α, β, γ	4·60	$1·68 \times 10^{9}$
Actinium-X	AcX	222	11·35 dys.	$7·07 \times 10^{-7}$	α	4·27	$1·64 \times 10^{9}$
Actinium emanation	AcEm	218	3·92 secs.	$1·77 \times 10^{-1}$	α	5·57	$1·79 \times 10^{9}$
Actinium-A	AcA	214	0·002 sec.	346	α	6·27	$1·86 \times 10^{9}$
Actinium-B	AcB	210	36·0 mins.	321×10^{-4}	β, γ	—	—
Actinium-C	AcC	210	2·15 mins.	$5·38 \times 10^{-3}$	α, β	5·15	$1·174 \times 10^{9}$
Actinium-C_2	AcC_2	210	—	—	α	6·4	—
Actinium-D	AcD	206	4·71 mins.	$2·45 \times 10^{-3}$	β, γ	—	—
Actinium-E	AcE	206	—	—	—	—	—

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14. The Transmutation of the Elements—Alchemy

Would to God all men might become adepts in our art, for then gold, the great idol of mankind, would lose its value and we should prize it only for its scientific teaching.—E. Philalethes (1651).

Alchemy appears to have been a mediæval system of philosophy, and it sought to demonstrate the validity of its doctrines concerning the cosmos by transmuting the baser metals into gold. The following excerpts from alchemical writings [1] will perhaps make clear their ideas on this subject:

Gold is the most perfect of metals because in it Nature has finished her work.—Roger Bacon (1214–1294).

The metals are all essentially identical, they differ only in form. Form brings out the

accidental causes which the experimenter must try to discover and remove.—ALBERTUS MAGNUS (1193–1284).

If by any reason the superfluous matter could be organically removed from the baser metals, they would become gold and silver. Our art only arrogates to itself the power of developing, through the removal of all defects and superfluities, the golden nature which the baser metals possess.—E. PHILALETHES (1651).

The mystic gnome who laboured in order to quicken the growth of the metals in mines was a creature of the superstition of the childhood of man. Even the general scepticism of G. Agricola did not protect him from a belief in these demons; and the *knoçkers* of the Cornish miners, until recently, were very real. G. Agricola wrote as if he knew all about them:

There is the gentle kind of gnome which the Germans as well as the Greeks call *cobalos*, because they mimic men. They appear to laugh with glee and pretend to do much, but really do nothing. They are called "little miners," because of their dwarfish stature, which is about two feet. They are venerable looking and are clothed like miners in a filleted garment with a leather apron about their loins. This kind does not often trouble the miners, but they idle about in the shafts and tunnels and really do nothing, although they pretend to be busy in all kinds of labour, sometimes digging ore, and sometimes putting into buckets that which has been dug. Sometimes they throw pebbles at the workmen, but they rarely injure them unless the workmen first ridicule or curse them. They are not very dissimilar to goblins, which occasionally appear to men when they go to or from their day's work, or when they attend their cattle. Because they generally appear benigh to men, the Germans call them *guteli*. Those called *trulli*, which take the form of women as well as men, actually enter the service of some people, especially the *Suions*. The mining gnomes are especially active in the workings where metal has already been found, or where there are hopes of discovering it, because of which they do not discourage the miners, but on the contrary stimulate them and cause them to labour more vigorously.

The, perhaps, more philosophical alchemists believed that the perfecting of the metals occurred spontaneously in the bowels of the earth, and Pliny, in his *De historia naturalis* (77 A.D.), tells us that exhausted mines have been closed down to enable the metals to fructify, and so be again profitably worked in a few years' time. They also believed that Nature aimed at the production of gold in mines, and that when she is hindered in her design, the so-called imperfect metals appear. The baser metals were hence called "diseased gold"; mercury was "ailing silver"; copper, iron, lead, and tin were "lepers" which, when cured of their leprosy, would become gold. The alchemists sought to find some means which would hasten the slow natural change so that the transmutation could be conducted in a much shorter time. "It is this means," said Roger Bacon, "which the alchemists indifferently called the elixir, the **philosopher's stone,**" etc.

The alchemists wrote in a language we do not now understand. They seem to have associated mystic extravagances with their operations, and to have described their processes in obscure ambiguous jargon, with the result that their readers were "stunned," as R. Boyle expressed it, "with dark and empty words." No wonder that J. J. Pontanus (1520) complained that after travelling through many countries to examine the claims of the adepts, he found many deceivers, but no true philosophers; and N. Lemery that "they professed an art the beginning of which was deceit, the progress of which was falsehood, and the end beggary." Alchemy thus fell into disrepute, for it seemed as if its claims could be established only by chicanery and fraud. Some of the more honest believers explained their failure by asserting that "the art of making gold is beyond the reach of human capacity, and it is made known by God to those alone whom He favours, and who are called adepts." At one period, however, the majority of alchemists did seek to make gold cheaply with the sole object of gaining untold wealth. Failure or delusion was inevitable. Accordingly, the alchemist often misrepresented the truth and degenerated into a charlatan and impostor, pretending, with vulgar frauds, that he had succeeded "in order," says M. M. P. Muir, "that he might really make gold by cheating other people," or else gain notoriety.

It is easy to understand how the belief that the base metals could be converted into gold dominated ancient and mediæval chemistry. Facts were cited in its favour.

The production of beads of silver and gold by the cupellation of metallic lead, and the reduction of metallic ores furnished direct evidence of the metamorphosis of the metals. Again, iron utensils in copper mines became coated with red copper when left in contact with the " mine water," so that the iron was seemingly transmuted into copper ; similarly, the formation of white and yellow alloys by mixing copper and certain earths, seemed with the then imperfect knowledge, ample proof of transmutation. The dogma of transmutation thus appeared eminently plausible ; it ran counter to no known laws of nature ; it rested upon no extravagant assumptions ; and it was sanctioned by the highest authorities. The immense labour which must have been expended in the fruitless pursuit of this chemical chimera by the alchemists is appalling. The quest was virtually abandoned with the advent of Lavoisier's balance.

Isaac Newton [2] gave vague hints of the mutual convertibility of rare and dense forms of matter in some bold speculations he made before the Royal Society in 1675. He said :

> Perhaps the whole frame of nature may be nothing but various contextures of some certain æthereal spirits or vapours, condensed, as it were, by precipitation, much after the same manner that vapours are condensed into water, or exhalations into grosser substances, though not so easily condensible; and after condensation wrought into various forms, at first by the immediate hand of the Creator, and ever since by the power of nature, which, by virtue of the command " increase and multiply," became a complete imitator of the copy set her by the great Protoplast. Thus, perhaps, may all things be originated from æther.

A possible dissociation of the elements has also been more or less vaguely suggested by B. Brodie, J. N. Lockyer, T. S. Hunt, F. W. Clarke, etc.

I. Remsen [3] has emphasized the fact that the alchemists were the working chemists of their day, and that they laid the foundations of experimental science. He further develops the idea that there is a life after the death of a good doctrine. The phlogiston theory lived in the form of the modern doctrine of free energy, and the idea that there is a relationship between the elements is what I. Remsen calls the spiritual part of alchemy which lives though alchemy is dead. The alchemist's dream of transmutation is very little nearer realization to-day than it was a thousand years ago, for no one has yet really succeeded in transmuting one chemical element into another other than by speculative argument. There is no unimpeachable evidence of a single transmutation of one element into another predetermined by man. Excepting the *interpretation* of the results of E. Rutherford's experiments described below, the words of M. S. Curie are applicable :

> En résumé, on peut considérer qu'il n'y a pas encore actuellement de raisons suffisantes pour admettre que la formation de certains éléments puisse être provoquée à volonté en présence de corps radioactifs. La production d'hélium reste acquise ; mais elle est reliée à une propriété essentielle des éléments radioactifs et n'est pas influencée par l'intervention de l'expérimentateur.

J. J. Thomson has also stated that all his efforts to decompose atoms by cathode rays or positive rays have failed to produce any conclusive evidence of a transformation. True enough, a few radioactive elements—radium, actinium, polonium, uranium, and thorium—seem to have been discovered in nature, and they are usually stated to be changing spontaneously from one elemental form to another ; but no process known to man is able to accelerate or retard, stop or start the metamorphosis. No element has yet been broken down into a simpler substance by a process controllable by man. In the words of Francis Bacon, *natura enim non nisi parendo vincitur*—nature to be conquered must be obeyed.

The alleged transmutation of copper into lithium and sodium by A. T. Cameron and W. Ramsay has been denied by M. S. Curie and E. Gleditsch and by E. P. Perman —the lithium and sodium were derived from the vessels used in the work ; the production of neon from radium emanation by W. Ramsay, and W. Ramsay and A T. Cameron has been denied by E. Rutherford and T. Royds—the neon was

derived from the air which had not been excluded from the apparatus; and the formation of carbon dioxide by the action of radium emanations on soln. of thorium and zirconium by W. Ramsay and F. L. Usher has been called in question by E. Rutherford—the carbon appears to have been derived from the grease used in lubricating the stopcocks. The alleged transmutation of hydrogen into neon, by W. Ramsay, J. N. Collie and H. S. Patterson, and I. Masson, by the action of a stream of cathode rays on hydrogen is considered by J. J. Thomson to be a mal-inference, since the neon is thought to be derived from that originally occluded by the electrodes, or glass vessel, and which is expelled by the bombardment of the cathode rays, but which cannot be removed by the mere application of heat. R. J. Strutt, T. R. Merton, A. C. G. Egerton, and A. Piutti and E. Cardoso could not verify the alleged conversion of hydrogen into neon. E. Briner records some negative attempts to transmute iodine vapour, or a mixture of hydrogen and helium by heating them in an electric arc; and R. W. G. Wyckoff's attempts to transmute lithium were likewise nugatory.

Intra-atomic energy.—The facts previously indicated show that not far from 2,000,000,000 cals. of heat are evolved during the degradation of one gram of radium. This is a quarter of a million times greater than is evolved by the combustion of a similar weight of coal. Hence it is inferred, from the atomic disintegration hypothesis of radioactivity, that the atoms of the radioactive elements, and probably also of other elements, have tremendous stores of potential energy, far greater than is developed during ordinary chemical reactions. The rate of degradation of the energy of the radioactive elements is comparatively slow, and is not available for doing useful work. The rate of evolution cannot be influenced by any known conditions and consequently the transmutation of the elements involves the discovery of methods of controlling these tremendous supplies of energy. Just as the application of a large quantity of electrical energy concentrated at the ends of a pair of platinum wires enabled H. Davy [4] to decompose the alkali metals, so W. Ostwald, W. Ramsay, and others infer: *if ever one stable element is transmuted into another element, a large quantity of energy in a highly concentrated condition will be required.* This is quite in harmony with the alleged dissociation of the elements in the hotter stars (*q.v.*), where but a few elements are present, and where the temperature has been estimated at 25,000°. The 3000°–4000° obtained in some electrical furnaces appear but puny in comparison with the tremendous natural powers present in the hotter stars. There is some evidence that the swifter α-rays can furnish the necessary energy for atomic disruption.

It has been pointed out that the formation of, say, gold from a metal atomically lighter, say tin, would require the expenditure of so much energy that even if the transformation were accomplished, it could not be a successful commercial process for the production of gold. On the other hand, the formation of gold from an atomically heavier metal, say lead, would liberate such an enormous amount of energy that the gold would be but an insignificant by-product, for the energy liberated during the process would have an enormously greater value than the metal. A. Schack discussed the thermodynamics of atomic energy.

The α-rays of high velocity are powerful agents in producing chemical reaction between molecules, but E. Rutherford has added some evidence that the α-particles can induce even more drastic changes in the atom itself. E. Rutherford,[5] and H. Geiger and E. Marsden studied the scattering of the α-particles as they pass through matter. In the case of the heavier atoms, like gold, the α-particle suffers no deflection, and the great rarity of large deflections led to the assumption that most of the atomic mass is centred in a relatively small, positively charged nucleus, and in a direct impact the α-particles approaches the nucleus to within about 3×10^{-12} cms. in the case of a heavy atom like that of gold. The large deflections are then attributed to the close impact of the α-particle with the nucleus of the atom—Fig. 3. With light atoms (i) the repulsion is less because of the smaller nuclear charge, and the α-particles can approach nearly ten times as close

as in the case of the more highly charged nuclei of the heavier atoms; and (ii) on account of the small mass of the lighter atoms, they are repelled to greater distances than the heavy ones, and in some cases projected beyond the range of the impelling α-particles. C. G. Darwin concluded that *all light atoms with a single positive nuclear charge, up to and including oxygen, should be repelled by a doubly charged α-particle in the same medium.* If the repelled atom has a double nuclear charge, no atom heavier than helium could be repelled beyond the range of the α-particle without obtaining energy from some other source. E. Marsden estimated that the nuclear encounter of an atom with an α-particle should repel the hydrogen atom with a velocity 1·6 times that of the α-particle; the range of the hydrogen atoms should be four times that of the α-particle; and its kinetic energy 0·64 of that of the α-particle. He was able to detect the propulsion of the hydrogen atoms beyond the range of the α-particle. H. Baerwald, and I. R. Seeliger have discussed the action of α-particles on matter.

E. Rutherford followed up the subject, and showed that the number of hydrogen atoms projected forward by an α-particle of 7 cms. range is thirty times greater than is required by the simple theory of scattering; and this was explained by assuming that the nucleus is distorted by the close approach. In traversing one cm. of hydrogen about 10^5 α-particles propel one swift hydrogen atom, or, out of 10^9 hydrogen atoms ionized, one is propelled forward at a high velocity as a result of direct nuclear impact. The charge of the swift hydrogen atoms is unipolar and positive, and the maximum velocity is in accord with theory, *viz.* 1·6 times that of the α-particle. Nuclear impact is an atomic phenomenon, and is produced either with an element or with its compounds. It is very difficult to eliminate water-vapour, and possibly other hydrogen compounds, from the field of action; and, in consequence, every source of α-radiation produces some hydrogen atoms moving at a high speed. There is also the possibility that hydrogen particles are shot from the radioactive element much as the α-particles are emitted, but there is no other evidence to support this hypothesis.

E. Rutherford investigated the effect with nitrogen and oxygen gases as well as with hydrogen. Assuming that singly charged particles are formed as a result of the impact, the swift nitrogen atoms should have a range 1·33 times, and the swift oxygen atoms a range 1·12 times, that of the impelling α-particle. The observed range for nitrogen corresponded with theory, but the range for oxygen was little different from that for nitrogen. G. S. Fulcher showed that the swift particles were not likely to be singly charged oxygen or nitrogen atoms because it is not likely that the orbital electrons would be borne along with the impelled atom. It is assumed that the forces binding these electrons to the nucleus are not sufficient to overcome the initial inertia at the moment of impact when they would have to take up a velocity of 10^9 cms. per sec. in less than 10^{-18} secs. Under these conditions it is probable that these electrons would be left behind, or else they would soon be brushed off by contact with the molecules of the gas being traversed. If the swiftly impelled particles were nitrogen or oxygen atoms with multiple charges their range would be shorter than the observed values. G. S. Fulcher therefore assumes that the swiftly impelled particles are really α-particles produced by the disruption of the nitrogen atom by impact. As in radioactive changes, during the atomic convulsion the internal atomic energy becomes available, and it enables the doubly charged helium atoms to be projected beyond the range of the bombarding α-particle. The observed fact is that moving particles are impelled by α-rays, the interpretation by G. S. Fulcher is that the atomic nucleus of a small fraction of the atoms bombarded by α-rays is entirely disrupted into α-particles. The phenomenon thus represents a kind of **artificial radioactivity.**

E. Rutherford placed radium-C as a source of intense α-rays in a metal box, 3 cms. from the end; an aperture in the box was covered by a silver plate eq. in stopping power to 6 cms. of air; and a zinc sulphide screen was placed about 1 cm. distant from the silver plate. If the box be exhausted, the number of scintillations

per sec. on the screen increases; if dry air or carbon dioxide be introduced, the number of scintillations per sec. increases in the ratio to be expected from the increased stopping-power of the 3 cms. gas column; but if nitrogen from different sources—nitrogen, boron nitride, sodium nitrate, titanium nitride, and paracyanogen—be introduced, the number of scintillations per sec. increases beyond this amount. It is assumed that hydrogen atoms are driven from the nitrogen atoms by the α-rays, because the observed range was too great for the masses of these particles to be greater than those of hydrogen atoms. Hence, it was inferred that **the nitrogen atom is disrupted by being bombarded with α-rays, and that one product of the action is a swiftly-impelled hydrogen atom.**

The deduction that **the long-range particles of nitrogen bombarded by α-rays are hydrogen atoms** is confirmed by estimates of the mass from the magnetic deflection of the particles. E. Rutherford further estimated that in the case of nitrogen only one α-particle in 300,000 succeeds in getting near enough to the nucleus to liberate a swift hydrogen atom with sufficient velocity for it to be detected; and if the entire α-radiation of a gram of radium were absorbed by nitrogen, it would generate about 0·0000005 c.c. of hydrogen per year! E. Rutherford added: It may be possible that the collision of an α-particle is effective in liberating hydrogen from the nucleus without necessarily giving it sufficient velocity to be detected by scintillations. If this should prove the case, the amount of disintegration may be much greater than this estimate.

It would be a bold chemist who would claim to be able to clean his products free from hydrogen or its compounds to anything approaching the implied degree of purity. E. Rutherford and J. Chadwick, however, stated that while the bombarding α-particles have a range of 7 cms., the swiftly moving hydrogen atoms obtained from hydrogen gas and hydrogen compounds have a maximum range of 29 cms. in air, while those from nitrogen have a range of 40 cms. This is taken as evidence that the swiftly moving particles cannot arise from the contamination of nitrogen with hydrogen.

The short-range particles obtained by the action of α-rays on oxygen and nitrogen are thought to be doubly charged helium atoms, and not singly charged or hydrogen atoms; but, instead of the helium particles having a mass 4, their at. wt. is 3. These particles were therefore assumed to belong to an isotope of helium. No long-range particles corresponding to those of mass 1, obtained with hydrogen and nitrogen, were furnished by oxygen; particles of masses 2 and 3 were driven from the oxygen, carbon dioxide, and sulphur dioxide, and E. Rutherford accordingly suggested that the oxygen nucleus is composed of four sub-atoms each of mass 3 and one of mass 4, these with two nuclear or binding electrons giving a net positive charge of 8. The nucleus of nitrogen is similarly composed of four doubly charged helium atoms of mass 3, two singly charged hydrogen atoms of mass 1, and three binding electrons giving a net positive charge of 7. The nucleus atom of carbon is supposed to be made up of four sub-atoms of mass 3 and charge 2, and two binding electrons. M. C. Neuberger calls the assumed element of mass 3—that is, E. Rutherford's X_3—*isohelium;* and he estimates the most probable value of its at. wt. to be 3·0011, corresponding to the at. mass $4{\cdot}95 \times 10^{-12}$ grms.

There are two possible modes of disruption of nitrogen, one giving swift doubly charged atoms of mass 3, and the other giving swift atoms of mass 4. Since the number of the former exceeds the latter five- or ten-fold, it is assumed that the two modes of disruption are independent and do not occur in the same atom.

According to this hypothesis, the atoms of the carbon, nitrogen, and oxygen contain sub-atoms of mass 3; in addition, there are, in the case of nitrogen, substances of mass 1, and in the case of oxygen there is a sub-atom of mass 4. In the case of nitrogen, experiment shows that the sub-atoms of mass 3 are more readily hit and dislodged by the α-particles than the more secluded hydrogen sub-atoms. The results indicate that the elements are built up of nuclei with 1, 2, 3, and 4 atoms,

with even greater masses functioning as secondary units. The nuclei of masses 1 and 2 each carrying one charge are regarded as hydrogen isotopes; those with mass 3 and 4 each carrying two charges are regarded as helium isotopes. E. Rutherford and J. Chadwick found that the long-range particles from aluminium carry a positive charge, and are deflected in a magnetic field to the degree to be anticipated if they are hydrogen nuclei moving with a velocity estimated from their range. E. Rutherford added:

On present views, the neutral hydrogen atom is regarded as a nucleus of unit charge with an electron attached at a distance, and the spectrum of hydrogen is ascribed to the movements of this distant-electron. Under some conditions, however, it may be possible for an electron to combine much more closely with the H-nucleus, forming a kind of neutral doublet. Such an atom would have novel properties. Its external field would be practically zero, except very close up to the nucleus, and in consequence, it should be able to move freely through matter. Its presence would probably be difficult to detect by the spectroscope, and it may be impossible to contain it in a sealed vessel. On the other hand, it should enter readily into the structure of atoms, and may either unite with the nucleus or be disintegrated by its intense field, resulting possibly in the escape of a charged H-atom or an electron of both.

R. A. Millikan and co-workers said that the passage of an α-ray through hydrogen, carbon, oxygen, nitrogen, chlorine, iodine, and mercury in at least 99 cases out of 100, and probably in all, results in the detachment of a single negative electron from a molecule or an atom. E. Rutherford and J. Chadwick found that the long-range hydrogen particles were furnished by fluorine, aluminium, phosphorus, boron, and sodium; but the numbers from the last two elements were less than from the other three. The following elements were bombarded, but very little if any effect was observed—lithium, beryllium, carbon, oxygen, magnesium, silicon, sulphur, chlorine, potassium, calcium, titanium, manganese, iron, copper, tin, and gold. They added:

It is of interest to note that no effect has been observed in the pure elements—*i.e.* those without isotopes such as carbon, oxygen, and fluorine, the atomic mass of which is given by $4n$, where n is a whole number. The effect is, however, marked in many of the elements the mass of which is given by $4n+2$, or $4n+3$. Such a result is to be anticipated if atoms of the $4n$-type are built up of stable helium nuclei, and those of the $(4n+m)$-type of helium and hydrogen nuclei. . . . No particles have so far been observed for any element of mass greater than 31. If this proves to be general, even for α-particles of greater velocity than those of radium-C, it may be an indication that the structure of the atomic nucleus undergoes some marked change at this point; for example, in the lighter atoms, the hydrogen nuclei may be satellites of the main body of the nucleus, while in the heavier atoms, the hydrogen nuclei may form part of the internal structure. The mass of a helium nucleus is less than that of the four hydrogen nuclei from which it may be supposed to be formed, by an amount $dm = 4 \times 1{\cdot}0077 - 4{\cdot}002 = 0{\cdot}029$. This corresponds with a loss of energy during the condensation of the hydrogen nuclei of $0{\cdot}029 V^2_\infty$ per gram atom of helium formed (V_∞ = velocity of light). Consequently, it is unnecessary to suppose that helium nuclei pre-exist in the nuclei of radioactive elements in order to account for the kinetic energy possessed by α-particles, for part of the energy liberated during the formation of helium nuclei within the atom from pre-existing hydrogen nuclei might be utilized in detaching the α-particles so formed and imparting to them their momentum.

H. Elbertshagen suggested that the atoms of a highly compressed monatomic gas of high at. wt.—*e.g.* mercury—might be shattered into their components by sparking between electrodes of the highest possible potential. It will be observed that in E. Rutherford's case the disruption is really an inference, since the products have not been isolated in the chemist's meaning of that term. E. Rutherford's test is extremely sensitive, and the trouble with a test like that proposed by H. Elbertshagen, would be to find if anything had happened.

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CHAPTER XXVII

THE ARCHITECTURE OF THE ATOM

§ 1. The Mutability of the Elements ; and the Disintegration of Atoms

To inquire whether the metals be capable of being decomposed and composed is a grand object of true philosophy.—H. DAVY (1811).

We must fight against the soporific influence of sham definitions. Especially must we guard against ever allowing them to stand in the way of an inquiry into facts.—A. SIDGWICK.

From the earliest traceable cosmic changes down to the latest results of civilization, we shall find that the transformation of the homogeneous into the heterogeneous is that in which progress consists.—H. SPENCER.

IN 1888, A. Grünwald [1] defined chemical atoms as follows :

A chemical atom is a complex of exceedingly many movable particles, which are elastic, but so intimately connected together that no chemical process which comes under our consideration is capable of severing this union and breaking the atom into fragments. The parts of the atom are not conceived of as absolutely immutable any more than the atom itself, but as capable within finite limits of undergoing modifications, which have definite relations to their mutual reactions.

This statement is very near what would be written to-day as an introduction to modern views on the structure of the atom. Near the close of the nineteenth century, G. le Bon [2] suggested that Becquerel's rays are due to the emission of particles which attends the liberation of *l'énergie intra-atomique* owing to *la dissociation de la matière*. This type of hypothesis is that generally employed at the present day. Many objections were raised at first. It was said that if atoms disengage heat in the process of self-destruction, they are endothermic and, by analogy, should be excessively unstable ; on the contrary, the atoms are the most stable things in the universe. P. Painlevé added that a combination which is so extraordinarily stable, and yet so extraordinarily endothermic, is something which contradicts not only the principle of the conservation of energy, but the whole body of facts which up to recent times have been scientifically established. A. Gautier, and A. Despaux argued in an analogous way.

Near the beginning of the twentieth century, many hypotheses were suggested to explain the phenomena associated with radioactivity :

J. Perrin [3] likened an atom to a miniature planetary system, and assumed that atoms more distant from the centre might escape from the central attraction and produce the phenomena of radioactivity. H. Becquerel assumed atoms to consist of positively and negatively charged particles moving in a system with different velocities, and when projected from the system gave rise to radioactivity. P. Curie at first regarded the emanation of radium as immaterial, consisting of centres of energy attached to gas molecules. P. and M. S. Curie assumed each atom acted as a constant source of energy which was derived from the potential energy of the atom, or the atom might act as a mechanism which instantly regained from the surrounding air the energy it had lost. P. Curie and A. Laborde assumed the heat energy might be derived from the breaking up of the radium atom, or from energy absorbed by radium from some external source. J. J. Thomson suggested that that energy was derived from a change within the atom—the contraction of the atom, for instance, would release a large store of energy. W. Crookes pointed out that if the moving molecules of the air impinged on the molecules of the radioactive substances, and were released with a lower velocity, the energy of radioactive substances could be derived from the atm. F. Re suggested a theory in which the contraction of nebulous matter formed atoms with the evolution of energy, and he likened an ordinary atom to extinct suns, while the atoms

of radioactive matter represented a transitional stage. Lord Kelvin suggested that the radioactive matter absorbed unknown radiations from the surrounding air. Analogous suggestions were made by O. J. Lodge, A. Schuster, E. J. Mills, N. Hesehus, J. K. Puschl, and J. W. Mellor. H. E. Armstrong and T. M. Lowry indicated that radioactivity might be an exaggerated form of phosphorescence or luminescence with a slow rate of decay. R. Meldola suggested *the helide hypothesis of radioactivity*. In this, the radioactive elements are supposed to be compounds of helium with other elements—**helides**—and these compounds are further supposed to be undergoing a gradual spontaneous decomposition into simpler substances. This hypothesis was soon abandoned by R. Meldola. J. M. del Castillo advocated a modified form of the same hypothesis, but it has recived very little consideration.

Attention has been mainly focused upon an hypothesis, which runs somewhat as follows : Ordinary atoms are small intricate systems of electrons, linked together by forces of tremendous power. The properties of the different elementary atoms are determined by the number and configuration of the infra-atomic electrons. Radioactivity is an atomic property, and it is an effect of the instability of certain atomic systems. The disintegration of the unstable atoms is marked by the emission of rays. The radioactive elements are therefore unstable, and are continually and spontaneously changing by numerous intermediate stages into more stable elements. This hypothesis is sometimes called E. Rutherford and F. Soddy's **theory of the disintegration of the atoms,** because they established its claim to serious consideration, and have done valuable work with its aid. Their hypothesis is now orthodox and fashionable. If this hypothesis should survive that struggle for existence which all neoteric hypotheses must undergo, then radioactivity will be cited as proof of the **devolution of the elements.** Astro-spectral observations leave little room for doubt that in the cooling stars a process of **evolution of the elements** is in progress. This subject has been discussed by J. H. Vincent.

It is further assumed that the radioactive elements are not unique among the elements in containing abnormal stores of internal energy, but—excluding potassium and possibly rubidium—the other elements are either immutable or else they are changing so slowly that no signs of mutation have yet been detected. According to the atom disintegration hypothesis of radioactivity Nature is continually changing the elements with the largest at. wt. such as uranium (238·5) and thorium (232·4) into simpler elements. The latter, in turn, are said to be stable simply because no signs of radioactivity have yet been detected. It is possible that if ever elements existed on earth with larger at. wt., and by inference, with more complex atoms, they have all degraded into simpler forms, and are now probably **extinct elements,** hence, also, it might be inferred that *the most widely diffused elements have small atomic weight*. The gaps which appear in the periodic table also appear significant. The elements with the smallest at. wt., and those which are found in greatest abundance on the earth—hydrogen, helium, calcium, oxygen, sodium, silicon, etc.—are usually considered to be the most stable, and to contain least infra-atomic energy. Hydrogen and helium, occurring in the hottest stars, are supposed to have a tendency to form aggregates, and pass into common terrestrial elements during the cooling of the hot stars. It seems as if uranium and thorium must have been exposed to peculiar conditions—possibly of press. and temp.—whereby they were elaborated beyond the limits of stability, and absorbed stores of energy which are now being slowly released because the conditions necessary for their stability no longer obtain.

It might be asked why the comparatively conspicuous self-destructive activities of radium have not led to its extinction long ago ? E. Rutherford estimated that the radium now on earth will be disintegrated and the whole virtually extinct in about 25,000 years. There can thus be little doubt that if there had not been a continuous source of supply, radium would have been an extinct element long ago. The decay of the heaviest known element uranium is so extraordinarily slow that it can just be detected, and a rough estimate made of its life—8,000,000,000 years—as indicated above.

The mode of evolution of the elements hypothecated in the attempt to co-ordinate the results of the spectroscopic study of stars and nebulæ, seems to be

supported by a mass of cumulative evidence, and to be inherently probable. It remains to find an adequate explanation to account for the vast stores of energy available in the hotter stars.

We can now see a possible explanation for the inseparable companionship of many elements. The occurrence or distribution of the elements over the earth appears to be an effect of an important genetic law. The approximately uniform quantities of many of the rarer metals in different parts of the earth indicate that these elements are degradation products of more complex elements; and that they, in turn, will probably be degraded into simpler products. The relative speeds of these slow changes determine the amount of each element which can be present on the earth at any given time. This subject has been discussed by W. D. Harkins, J. Waddell, etc.

It may very properly be thought that *a modicum of fact is here entangled with an abnormal amount of speculation*, especially when it is remembered that the experiments have been made upon very minute quantities of material. At first sight, it does appear as if we have developed what A. Smithells [4] humorously called "a chemistry of phantoms." Thanks, however, to the extraordinary delicacy of the electrometer and of the spectroscope, there is no doubt about the facts, even though but extremely minute quantities of radium are available for experiments. The argument converges on the assumption that radioactivity is an atomic property; this hypothesis, in turn, is mainly based on the indifference of the speed of radioactive changes to external conditions of temp., press., etc. It is therefore pertinent to inquire into the validity of the alternative hypothesis, and ask:

Are the "radioactive elements" really elements, or are they compounds containing helium? As already hinted, the dogma that radium is an element is not so firmly established that there are no reasonable grounds for the exercise of some Cartesian doubt, for, said E. W. Morley, he is wise whose assertions regard the possibility of finding at some time evidence to the contrary. E. Rutherford has said that "since in a large number of cases the transformation of the atoms is accompanied by one or more charged atoms of helium, it is difficult to avoid the conclusion that the atoms of the radioactive elements are built up, in part at least, of helium atoms." As an alternative to Rutherford's atom-disintegration hypothesis, and as a corollary to the inference that the molecules of the argon-helium family are really polyatomic (**1.** 13, 9), the helide hypothesis assumes that radioactive elements are really compounds of an active form of helium in the same sense that nitrogen chloride may be said to contain the atomic or active form of nitrogen. Ordinary helium, like ordinary nitrogen, is characterized by great chemical inactivity. If this hypothesis be valid, it must be supported by a formidable list of unique hypotheses, for it must be assumed further that (1) the alleged compound—**helide**—is spontaneously decomposing; (2) abnormally large amounts of energy are set free during the decomposition; (3) the emission of radiations accompanies the change; (4) the speed of the decomposition is not affected by any known external conditions; and (5) in opposition to a little circumstantial evidence, that the helium molecule is a complex of atoms, and not monatomic. *Otherwise*, adds H. E. Armstrong: the decomposition of radium regarded as a compound of atomic helium is no more remarkable than that of liquid ozone, or of nitrogen chloride! H. E. Armstrong continues:

> The atoms of helium and of the allied inert gases are gifted with intense activity far beyond anything we know of, it may well be that when such atoms enter into combination, either with one another or with other elements, the amount of energy set free is very great, and that when they combine with other materials, they may produce changes in properties very different from and far more profound than those we know of at present.

The plausibility of the helide argument turns on this: The greater the amount of hypothetical energy assumed to be required to break down the hypothetical helide molecule into its supposed atoms, the greater the appearance of probability of the argument that radioactive phenomena are chemical in kind. Questions

like these have to be treated more by instinct (or prejudice) than by logic ; and those who do the work must use what hypotheses they find most fruitful.

Naturally, the student of chemistry may be somewhat disconcerted with this apparent attack on what appear to be the essential principles of chemistry. At first sight, it does seem as if we must say " good-bye to the equations of chemistry," because, if the truth about the suspected disruption of atoms be truly vindicated, the fundamental concepts—atom, element, persistence of weight, etc.—must be revised in order to make them harmonize with the facts. The conception of an **element,** given in the first volume, has long held an honoured place in chemical text-books ; and, with this before us, at first sight, it might appear illogical to apply the term to a substance which can be resolved into two or more simpler forms of matter. Any substance which can furnish two or more different elements may seem to have forfeited its place in the list of elements. Some try to evade the difficulty by assuming that there is an agreement among chemists to recognize a substance as an element which, under proper conditions, exhibits a spectrum showing characteristic lines possessed by no other element, and possesses a definite combining weight. Of course, we are at liberty to change our definitions, but, as W. D. Bancroft has said, the only advantage of the new definition is that it enables chemists to say that they have decomposed an element. M. S. Curie stated definitely that radium is not a compound of helium, but the only way she can make radium an element is by changing the old definition so that it shall not include radium. The definition employed in the first volume, however, is elastic enough to cover cases of transmutation, for, *if an element containing but one kind of matter suffered an atomic cataclysm, it might furnish two or more different kinds of matter each of which would be an element because it would contain but one kind of matter.* K. Fajans suggests the definition : " An element is a substance which has not been separated into simpler constituents and is not known to be a mixture of other substances." Each isotope, on our standard definition of an element, is to be regarded as a definite element ; but if, as is done by F. Paneth, " an element is defined as a substance which cannot be simplified by any chemical process," then isotopes would be regarded as one and the same element, because they cannot be separated ; and a specific at. wt. is not then a characteristic property of an element. F. Paneth further added that an element can consist of similar atoms—*Reinelements, pure elements*—or of atoms differing in weight or radioactivity, or both—*Mischelements, mixed elements.* Some one has suggested that the elements be called *chemical primaries.* We are always loath to multiply definitions, and would much rather condense a number of definitions into one. As already emphasized, the definition must not be taken to imply that the elements are absolutely immutable, although, so far as our present knowledge goes, they are both immutable and primitive in chemical reactions. This subject has also been discussed by R. Wegscheider, and J. Barborovsky.

However paradoxical it may seem, the hypothesis that the **atom** of an element is a most intricate bit of mechanism, a complex aggregate of parts liable to disruption, is now generally accepted. This, however, does not affect the time-honoured definition of an atom. **The atom still remains a veritable unit indivisible in chemical reactions.** Had the facts, speculations, and theories here discussed been treated at the beginning of the first volume, that would not have altered our mode of presenting the facts of material chemistry. According to T. W. Richards, so far as ordinary chemical reactions are concerned :

> Our relations with chemical elements primarily concerning us are unchanged by all the fascinating new knowledge. These same old elements remain as permanent as ever they were. . . . The atomic theory is indeed even more convincing to-day with regard to mundane chemical affairs than it was before the dawn of radioactivity.

Suppose an atomic convulsion or cataclysm were to occur so that the complex system of electrons which is supposed to form an atom were to break up into simpler parts ; suppose further some of the electrons grouped themselves into helium, and

the others into some other substance ; and let us also assume, for a moment, that some electrons simultaneously escape and are merged into the æther of space, it is then conceivable that there will be an apparent loss of weight. Consequently, while *the law of persistence of weight holds good with chemical reactions in which the atoms remain intact*, it is quite conceivable that an apparent loss in weight *might* occur during a radioactive change. The evidence, however, is in favour of the assumption that the law holds good in radioactive changes. The relation of mass to energy is treated in **1.** 13, 1. If the products of the disintegration of the atom have mass, it might be inferred that the absolute mass still remains constant, although, if radium be an element, the invariability of mass or weight can no longer be referred back to the constancy of the atom. This visionary phenomenon has been described in order to emphasize the need for care in building rigid, non-plastic concepts and definitions from negative results based on the uncontradicted experience of mankind.

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§ 2. The Creation and Annihilation of Matter

Even if we resolve all matter into one kind, that kind will need explaining. And so on for ever and ever deeper and deeper into the pit at whose bottom truth lies, without ever reaching it. For the pit is bottomless.—O. HEAVISIDE.

Things which are seen were not made of things which do appear.—ST. PAUL.

Æther is the parent of all things.—LUCRETIUS (*c.* 60 B.C.).

In mechanics, the definition of matter is based upon Newton's first law of motion —the law of inertia—where matter is defined as that which requires the expenditure of an external force to change its state of motion. Otherwise expressed, inertia, or helplessness, is a characteristic of every form of matter. No material thing can of itself change its own state of motion, for an external influence is required before such a change can take place. If it be admitted that **any entity which requires the application of a force before it can change its state of motion is a form of matter,** an electron in motion must be a form of matter, because it requires the application of a force to change its state of motion.

The inertia of matter.—This definition is also reversed, and **force is defined to be that influence which is required to change the velocity of any material body,** and it is measured in terms of the **dyne** as unit. A dyne is that force which applied

to a mass of one gram during one second imparts to it a velocity of 1 cm. per sec., or which changes the velocity of the body 1 cm. per sec. when acting for 1 sec. These ideas can be expressed in another form. The inertia of a body is that property of matter which resists change of motion, and it is measured in terms of the force required to produce a change of 1 cm. per sec. in the velocity of the body. Accordingly, *when the action of a force on two bodies produces the same change of velocity per second, their inertia are said to be equal.*

The mass of matter.—A body falling from a height down to the earth's surface —*in vacuo* so as not to be influenced by the resistance of the air—gains in velocity, say, g cm. per sec. If the mass of the body be m, then the force pulling that body down will be measured by the product mg. This is the **weight** of a body; hence the weight of a body is g times its mass. The weight w of a body measures the force by which it is attracted to the earth's surface, whereas mass refers to the quantity of matter m in a body, and is independent of gravitation or weight. Experiments have shown that all material bodies have the same numerical value for g, namely, 981 cms. per sec. when acting for 1 sec. (latitude 45°, and at sea-level). Accordingly, $w=981m$; or the weight of 1 grm. of matter is 981 dynes; or the weight of a body is 981 times its mass; or the mass of a body is $\frac{1}{981}$ of its weight—under standard conditions. The masses of two bodies in the same place must therefore be proportional to their weights. *If in the same locality the action of gravity on two bodies produces the same change of velocity per second, their masses are said to be equal.* This conclusion is in harmony with that deduced in the preceding paragraph, and, accordingly, it has been inferred that **mass and inertia are identical;** meaning that the definitions of inertia and of mass, in the nomenclature of mechanics, are not mutually exclusive.

Electromagnetic mass.—When charges of electricity are set in motion, they act like electric currents, and set up magnetic fields which oppose the motion—E. Lenz's law.[1] An electrically charged body exerts force all round itself, a greater force is required to stop or accelerate an electrically charged particle than when not charged. Otherwise expressed, the inertia of a particle, or its effective mass, is greater when electrically charged. Consequently, *an electrified particle possesses in virtue of its electrical charge, a supplementary inertia of electromagnetic origin.* According to J. J. Thomson, the simple dynamic energy of a charged sphere is $\frac{1}{2}m_1V^2$, where m_1 is the mass, and V the velocity; the supplementary energy required for the magnetic field introduced by a charged sphere of unit radius is $\frac{1}{3}e^2V^2$, where e denotes the electric charge. Adding dynamic and magnetic energies, it follows that the

$$\text{Total energy} = \tfrac{1}{2}(m_1+\tfrac{2}{3}e^2)V^2$$

in which the bracketed term is the effective mass, the energy of the combination; the term $\frac{2}{3}e^2$ is the electric inertia or electromagnetic mass.

Again, when two charged spheres are in rapid motion with the same speed in the same direction, the forces which they exert on one another are equal and opposite; but in all other cases, the force which A exerts on B is not equal and opposite to that which B exerts on A. It is therefore assumed that A and B are in communication with another system, the æther, which is able to store momentum so that when the momentum of the system AB is altered, the momentum which has been lost by A and not gained by B has been stored in the æther. Only when A, B, and the æther are considered as one system can the momentum be regarded as constant. Thus do the experiments of M. Faraday show that *a certain proportion of electrical energy can be located outside matter.* With M. Faraday's conception of tubes of force, endowed with momentum, the energy of a tube of force will belong to the body from which the tube originates; and the electric inertia will be due to the grip of these tubes of force on the æther. In this sense, as J. J. Thomson puts it, *an electrified body is asoociated with an œthereal or astral body which it has to carry with it as it moves, and which increases its apparent mass.*

J. J. Thomson further showed that when an electrified sphere is in rapid motion, the lines of force have a tendency to set themselves at right angles to the direction in which they are moving; they tend to leave the front and rear, and to crowd into the middle. This increases the electrical potential energy; but the mass of the æther bound by the lines of force is proportional to the electrical potential energy; hence, the electrical mass of a charged sphere in motion will be greater than when the sphere is at rest. The difference is very small when the velocity of the charged body is small, but when the speed approaches that of æther wave motion, the lines of force become equatorial, and the mass indefinitely large. W. Kaufmann tested these deductions with the fast-moving β-particles from radium. He measured the ratio of the electric charge e to the mass m of its carrier for speeds ranging from $2{\cdot}36\times10^{10}$ to $2{\cdot}83\times10^{10}$ cms. per sec. Several relations between the mass and speed of the moving particles have been deduced—by J. J. Thomson, O. Heaviside, G. F. C. Searle, etc.—on the assumption that the moving electrode is either (*a*) rigid, or (*b*) contractile. W. Kaufmann employed the one deduced by M. Abraham, for rigid electrons, *viz.*

$$\frac{m}{m_0}=\frac{3}{4}\cdot\frac{1}{\beta}\left(\frac{1+\beta^2}{2\beta}\log\frac{1+\beta}{1-\beta}-1\right)$$

where m denotes the mass of the electronic particle moving with a velocity V; m_0 denotes the mass of the electron for slow speeds; and $\beta=V/V_\infty$, where V_∞ represents the velocity of light. W. Kaufmann's results are shown in Table I.

TABLE I.—EFFECT OF VELOCITY OF MOTION ON THE ELECTRICAL MASS OF A PARTICLE.

$V\times10^{-10}$	$\frac{e}{m}\times10^{-7}$	m/m_0	
		Observed.	Calculated.
2·36	1·31	1·50	1·65
2·48	1·17	1·66	1·83
2·59	0·97	2·00	2·04
2·72	0·77	2·42	2·43
2·83	0·63	3·10	3·09

Hence, either the value of m *increases* or the charge e *decreases* with increasing velocity, for the greater the velocity the smaller the numerical value of the ratio of the electric charge to the mass. The relation

$$\frac{m}{m_0}=(1-\beta^2)^{-1}$$

deduced by H. A. Lorentz for an electron which contracted in the direction of its translatory motion without changing its other dimensions, did not give such good results; but, as M. Planck has emphasized, the experiments probably agree with both formulæ within the limits of experimental error for the β-rays employed. A. H. Bucherer assumed that an electron is spherical when at rest, but when in motion contracts in the direction of its translation, and expands laterally so as to preserve a constant volume; he also tested the constancy of the ratio e/m for the β-rays, and found that the results agreed with the formula for the contractile electron, but not with that for the rigid electron.

W. Kaufmann assumed that the charges on the particles remain constant and invariable, and accordingly, it follows that the electromagnetic mass of the electrons is not constant, but increases rapidly as the velocity is augmented. The greater the speed, the greater the mass; he found that the electromagnetic mass of the

more rapidly moving particles was as much as three times that of the slower moving ones. On J. J. Thomson's hypothesis, this means that the mass of these particles is due to the æther gripped by their fields of force. Further, if any part of the mass of an electron is ordinary mechanical mass, it must be indefinitely small in comparison with that which is of electrical origin, since the electrical inertia of a body depends upon its velocity and approaches infinity when the velocity of the body approaches that of light. It is therefore inferred that if the premises be granted, it follows that the velocity of light is the greatest possible velocity which a body can attain; but no other valid reason has been given for the assertion. The variation in the electromagnetic inertia or mass of a body is the same as if the electrical mass existed alone, and the dynamical mass were virtually zero. Consequently, it has been inferred that (1) the electrons do not possess a material mass in the ordinary sense of the word; and (2) the electrons have no mass other than that which is derived from their motion and electrical charge. If the real mass of an atom is the sum of the positive and negative electrons, and the latter have no material mass, it might be inferred that the positive electrons or the mass of an atom would still remain a constant. H. A. Lorentz, however, has shown that in all probability the mass of all particles will be affected by their translational velocity to the same degree as the electromagnetic mass of the electrons.

If dE/dt denotes the rate at which a black body receives energy; F, the force; and V_∞, the velocity of light, J. C. Maxwell, L. Boltzmann, and E. L. Nichols and G. F. Hull showed that $F=V_\infty^{-1}(dE/dt)$, which is evidenced as the so-called press. of radiation. A body subject to the force of radiation, F, will acquire momentum, M, at the rate $dM/dt=F$, and hence $dE/dM=V_\infty$, meaning that the rate of acquired energy to the acquired momentum is equal to the velocity of light. By definition, momentum, M, is the product of mass into velocity, or, $dM=V_\infty dm$, and substituting for dM in $dE/dM=V_\infty$, it follows that $dm=V_\infty^{-2}.dE$, or, since V_∞ is known to be 3×10^{10} cms. per sec., *changes of mass are proportional to changes of energy:*

$$dm=1{\cdot}111\times10^{-21}dE$$

A similar result is obtained for the kinetic energy and mass of a moving body. Hence, *a body which is receiving or emitting radiant energy gains or loses energy in proportion, and by the amount* $1{\cdot}111\times10^{-21}$ *grms. for every erg.* This result obtained by G. N. Lewis is the same as that previously obtained by A. Einstein from the electromagnetic theory, and the principle of relativity. With the electromagnetic theory alone, D. F. Comstock obtained a similar result but involving a constant. If the mass of the body be a function of the total energy, any body will weigh more when hot than when cold; more when carrying an electric charge than when neutral; and more when in motion than when at rest. Granting these premises, 68,000 cals., or $2{\cdot}89\times10^{11}$ ergs of energy, are liberated in the formation of a mol of water; consequently, the change in mass which occurs in the formation of a mol of water is $dm=-3{\cdot}18\times10^{-9}$ grms. This is so small as to be outside the range of experimental verification. These results do not mean that the law of conservation of energy has failed, it is only when restricted systems are considered that there are actual losses; for the energy liberated by a change of mass goes to increase the energy and consequently also the mass of some other body.

Again, it is assumed that electricity is a phenomenon of the æther, and that the atom is built entirely of electrons; consequently, as J. Larmor expressed it: atoms are forms of æthereal strain, or **the material atom is formed entirely of æther,** and has no material substratum. Further, the electrons are supposed to be minute electrified strains, squirts, vortices, swirls, eddies, or whirlpools in the æther. When æther is condensed into vortices it is supposed to acquire a tension decreasing with the distance in all directions, and creating a mutual attraction between any two sets of vortices, which is directly proportional to the product of both the amounts of energy needed for their contraction (mass), and inversely proportional to the squares of the distance between their centres—*i.e.* Newton's formula for gravita-

tion. The intangible, imponderable, all-pervading æther is supposed to be susceptible to the solicitations of gravity, as matter, only when it is stirred into innumerable swirls, which are held together by powerful cohesive forces. Hence, it is said : *æther is the mother of matter ;* for in the æther—

Wrapt in mystic silences and glooms,
The slumb'ring secrets of creation lie.

Some even claim to have created material atoms from immaterial æther, but the claims are somewhat questionable. The stages in the alleged genesis and destruction of matter can thus be symbolized :

Material — Immaterial

Matter *en masse* ⇌ Molecules ⇌ Atoms ⇌ Electrons ⇌ Æther.

Dematerialization of matter ⇌ Materialization of æther.

When, therefore, it is assumed that material electrons have been resolved into primitive æther by relieving the strains, or stilling the swirls, it is at the same time assumed that matter can be deprived of cosmical existence, and transmogrified into Nirvanian nothingness. With the annihilation of ponderable matter, the law of the conservation of matter disappears, and apparently the only constant in the universe is nothingness !

The argument turns on the nature of the electrons and of the æther. The æther is assumed to be immaterial, or, as Pythagoras (*c.* 500 B.C.) expressed it, " a celestial substance free from all perceptible matter." It must be remembered that the æthereal plenum cannot be compared with any known thing. It is utterly beyond the range of our sense perceptions, and as G. le Bon has said, we are related to the æther much as a man born deaf is related to music, or a man born blind is related to colour ; accordingly, no analogy can make such men understand what is a sound or a colour. In the words of T. A. Edison (1892) : " As for the æther which speculative science supposes to exist, I know nothing about it."

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§ 3. Thomson's Corpuscular or Electronic Hypothesis of Matter

If we be curious to know what matter is, we plunge at once into that deep which surrounds us on every side, and which never yet was fathomed by human intellect.—J. F. DANIELL.
Liability to error is the price we have to pay for forward movement.—A. SIDGWICK.

No difference other than velocity of translatory motion has been detected in

the properties of negative electrons when produced in many different ways, and from many different gases; and since the mass of a negative electron (corpuscle) is less than that of any known atom, the corpuscle must be a constituent of many different substances; and the atoms of these substances consequently must have something in common. This suggests the idea that the atoms of the chemical elements are built of simpler components, the electrons have thus been regarded as the ultimate sub-atoms or the *Uratomen* of which matter is essentially composed. Since the electron is a constituent of atoms, J. J. Thomson [1] considers that "it is natural to regard the electron as a constituent of the primordial system."

J. J. Thomson's electronic theory of matter is one of the unitary theories. It is based on a suggestion made by Lord Kelvin, in a paper entitled *Aepinus atomized*, that a chemical atom consists of a sphere of uniform positive electrification containing negative electrons of much smaller dimensions embedded therein; it assumes that **each atom of any element consists of a large number of electrons, all electrified negatively, and held together by positive electricity equivalent in amount to the sum of the negative charges of all the electrons so as to produce an electrically neutral atom.** J. J. Thomson also accepts the atom-disintegration hypothesis of radioactivity.

TABLE II.

Total number of electrons.	Number of electrons in successive rings (numbered onwards).				
	1	2	3	4	5
4	4				
5	5				
6	5	1			
7	6	1			
8	7	1			
9	8	1			
10	8	2			
11	8	3			
..	..	..	..	..	..
16	11	5			
17	11	5	1		
18	11	6	1		
..	..	..	..		
31	15	11	5		
32	15	11	5	1	
33	15	11	6	1	
..	..	..	..	..	..
48	17	15	11	5	
49	17	15	11	5	1
50	18	15	11	5	1
..	..	..	..	..	..
58	19	16	13	8	2

The distribution of a number of negatively charged particles in a sphere of uniform density has been investigated mathematically by J. J. Thomson. Five is the greatest number of electrons which can be in equilibrium in a single ring. But if other electrons be placed within the ring, a larger number can be maintained in equilibrium in one ring. Thus a ring containing six electrons would not alone be stable, but if a seventh electron be placed within the hexoidal unstable ring, the system will become stable. A greater number of electrons will arrange themselves in a series of concentric rings. Table II illustrates the number of electrons arranged in a series of concentric rings which give systems in stable equilibrium when the number of electrons in the system ranges from 1 to 58. These suffice to illustrate the principle involved.

The idea was neatly demonstrated by repeating an old experiment due to A. M. Mayer [2] —the so-called **Mayer's floating magnets.** Small uniformly magnetized needles were thrust through discs of cork, and floated on water so that the negative poles of all the needles floated above the surface of the water while the positive poles were submerged.

FIG. 1.—Mayer's Floating Magnets.

When a positively charged magnetic pole is suspended a little above the surface of the water, these needles arrange themselves like J. J. Thomson's imaginary corpuscles. The diagram (Fig. 1) shows that a group of these needles arrange themselves in water at the apices of a triangle; a group of four needles, at the four corners of a square or as a triangle

with a needle in the middle ; if another needle be thrown into the water, the five needles take up positions at the corners of the pentagon or as a square with one in the centre ; if another needle be thrown in, five needles form a pentagon as before, but the sixth needle goes to the centre of the pentagon or a triangle with needles at the apices and mid-points is formed ; if another needle be introduced, six arrange themselves at the corners of a hexagon, and the remaining needle goes to the centre. Thus, a ring of six needles is unstable if hollow, but it is stable when another is placed inside. This is an important principle in the formation of stable systems of negatively charged electrons. It is obvious that *for stable equilibrium the structure must be substantial ; a system with a large number of electrons on the outside, and none within, will be unstable.* R. W. Wood obtained analogous results. A. C. Crehore suspended a number of steel balls of uniform size by means of long thin wires in castor oil, and then charged the balls up to a high potential and allowed them to take up their equilibrium position. The disposition of the balls agrees with that worked out by J. J. Thomson.

There is an important difference between Mayer's floating magnets, Thomson's systems of concentric rings of electrons, and the electrons in a real atom, because the two former are supposed to move in one plane (as on the surface of the water), whereas the electrons of an atom are in motion—possibly revolving in orbits like planets or they may vibrate about stable positions.

The architecture of the atom.—According to Lord Kelvin's hypothesis,[3] each atom is a remarkable constellation of electrons ranged in a system of concentric rings all assembled within a sphere of uniform positive electrification. J. J. Thomson showed that although the mass of the negative electron seems to be about $\frac{1}{1700}$th of that of the hydrogen atom, it cannot be assumed that the hydrogen atom contains about 1700 negative electrons, unless the mass of the positive electron be ignored. The surface of the imaginary sphere may be regarded as the limiting surface of the atom. The electrons are further assumed to be in rapid orbital motion about the centre of the sphere. They are subject to the mutual repulsion of the negative electrons and the attraction of the total positive charge. Positive electricity never appears apart from matter, so that it is always associated with the atom itself. J. H. Jeans, N. Bohr, G. A. Schott, etc., have studied the emission of series of spectral lines by atoms made up of rings of revolving electrons. H. Nagaoka assumed that the positive charge is concentrated at a point in the centre of the atom, and the charge is not then uniformly distributed over the sphere. As H. Poincaré expressed the idea : " The neutral atom may be considered to be composed of an immovable principal portion positively charged, round which move, like satellites round a planet, several negative electrons of very inferior mass." Fig. 2 gives but a crude notion of what is meant by concentric rings of corpuscles in rapid orbital motion about a central positively charged sphere.

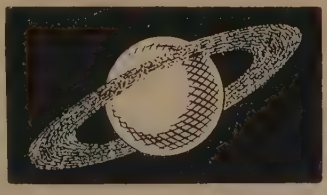

FIG. 2.—Diagrammatic Representation of one form of the Corpuscular Ring Hypothesis of the Constitution of an Atom.

The atom has thus been compared with the planet Saturn and its rings—**the Saturnian atom.** This intricate mechanism is supposed to represent the inner structure of the chemist's atom. The atoms, in turn, are supposed to be disposed in the molecule in an analogous manner. Consequently, the relation of the electrons to the whole molecule must be somewhat complex. The apparent hardness and impenetrability of the atom, so well emphasized by Isaac Newton, now appears to be a kind of gyrostatic equilibrium due to the rapidity of motion of the component electrons. We are told that a soft wax-candle fired from a gun can be shot through a deal board, and that the speed of the jets of water in hydraulic mining in California was so great that a man could not strike an axe into the water which had just left the nozzle. It is quite possible therefore that an atom may appear to be rigid owing to the rapid motion of the constituent electrons. " Hardness," it is said, " is merely softness in rapid motion."

One reason for postulating the Saturnian atom as a basis for investigation is rather

interesting. J. Plateau [4] spun little spheres of oil in a mixture of alcohol and water so that they rotated while suspended in the liquid. During their rotation, the little spheres flattened at their poles and bulged at their equators. When the speed of rotation of a sphere was great enough, rings of oil were thrown off. The rings broke and coalesced to form little spherules which rotated on their own axes and revolved round the parent sphere. This remarkable experiment has been used for illustrating a possible mode of formation of a solar system like ours from a contracting spinning nebula. The Saturnian atom is considered to be the figure of equilibrium of a mass of rotating electrons in a sphere of positive electrification. It is not difficult to understand how the "figure of equilibrium" of a rotating fluid cannot be spherical, for gravity is progressively neutralized in passing from the axes of rotation (the poles) towards the equator, where the mass is specifically lighter. The faster the spin the more oblate the spheroid, and in the extreme case, with an increasing speed of gyration, the spheroid must become either a flattened disc, or else, at some critical velocity, there must be an interruption in the process of flattening, and the spheroid must alter fundamentally in shape or break into pieces. H. Poincaré, G. H. Darwin, and J. H. Jeans have investigated the subject mathematically.

E. Rutherford and H. Geiger [5] found that when the α-particles from a radioactive substance encountered thin gold-leaf, most of the particles pass through with only a slight deflection; but every now and again, about one in 8000, one of these particles recoiled towards its source. The idea is illustrated by Fig. 3, which represents diagrammatically the hyperbolic paths of the α-particles in the vicinity of the positive nucleus. The phenomenon, known as *the scattering of the α-particles*, obeyed the same laws as the repulsion of an electric charge in motion by one at rest. From the amount of scattering, it was concluded that at some point in their paths these particles pass through a very intense electrostatic field caused by a positive charge, whose magnitude is approximately one-half the at. wt. of the metal through which the scattering occurs; and that the α-particle approaches the repelling positive charge within a distance which is infinitestimal as compared with the radius of the atom. The radius of an atom is approximately 10^{-8} cms., consequently, the α-particles must have approached the hydrogen nucleus so closely that their centres were only $1{\cdot}7 \times 10^{-13}$ cms. apart. Otherwise expressed, the α-particles penetrated within the atom of gold. Hence, also, E. Rutherford concluded that *the positive nucleus is an essential part of the mass of the atom, and has linear dimensions which are exceedingly small in comparison with the linear dimensions of an atom.* It is estimated that with hydrogen, the charge on the positive nucleus is $4{\cdot}7 \times 10^{-10}$ electrostatic units; the mass is $1{\cdot}6 \times 10^{-24}$ grms.; and the radius is $1{\cdot}0 \times 10^{-16}$ cms.; or, as P. Zeeman puts it, the diameter of the electron is $\frac{1}{40,000}$th part of the diameter of an atom; and in the solar system, the diameter of the earth is $\frac{1}{20,000}$th of the diameter of its orbit round the sun. Hence, if the earth represents an electron, an atom is a sphere having a sun as centre (positive nucleus), and a radius eq. to twice the distance of the earth from the sun.

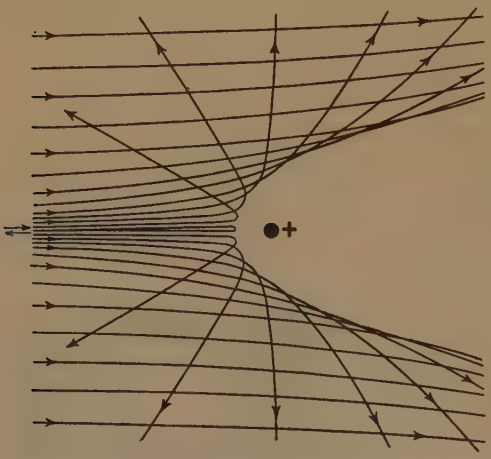

FIG. 3.—Paths of a Stream of α-particles in the Vicinity of the Positive Nucleus.

E. Rutherford, therefore, gave greater precision to the vague entity of positive electricity of J. J. Thomson's atom; he assumed that the atom—the so-called **Rutherford atom**—contains (i) a nucleus no larger than 10^{-16} cms. in diameter and charged with positive electricity. (ii) A cluster of negative electrons revolving about the central nucleus in orbital motion, each about 10^{-13} cms. in diameter.

(iii) An outer group containing but a few electrons rotating about the inner group and which are much less rigidly attached to the atom. To explain why the physical and chemical properties of the atom do not go hand in hand with X-ray and γ-ray phenomena, it is further assumed that (*a*) the other group of electrons are responsible for the physical and chemical properties of the atom—**valency or mobile electrons**; that (*b*) the inner group determines the phenomena associated with radioactivity; that (*c*) the positive nucleus mainly determines the mass of the atom, while the masses of the groups of negative electrons are but a small fraction of the at. wt.; that (*d*) the positive charge is numerically equal to the sum of the negative charges on all the electrons, so that the atom is electrically neutral; and that (*e*), relative to their size, the electrons are relatively about as far from each other and from the nucleus as the planets are distant from one another and from the sun.

N. Bohr was the first to represent the mechanism of the intra-atomic motion; he applied the quantum theory of radiation to Rutherford's model atom to calculate the size of the atom, and explained the series of lines found in the spectrum of some elements. The various electrodynamic complications which attend the motions of the electrons were disregarded in the first approximation, and the purely electrostatic attraction between the positive nucleus and the negative electron is considered. The motion of the electrons about the nucleus was treated as if the attractive forces followed the inverse square law, and the mass of the nucleus was treated as indefinitely large in comparison with that of the electron. The development of the theory depends on two simple theorems in elementary physics.

If a body, say an electron, of mass, m, is moving uniformly on a circular path of radius, r, with a velocity, V, while under the influence of a central force, the normal component of the force, *i.e.* the centripetal force, F, is given by the relation:

$$F = \frac{mV^2}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the potential energy of an electron with a charge, e, at a distance, r, from a nucleus of charge, E, is

$$\text{Potential energy} = \frac{eE}{r} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the electron revolves in its orbit, ω times per second,

$$V = 2\pi\omega r \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and if the force of attraction, F', between nucleus and electron varies inversely as the square of their distance, r, apart, then, as in the gravitation law:

$$F' = \frac{eE}{r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If the system is in equilibrium,

$$F = F'; \text{ or } \frac{mV^2}{r} = \frac{eE}{r^2} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and, from (2), (3), and (5),

$$\text{Potential energy} = m(2\pi\omega r)^2 = \frac{eE}{r} \quad . \quad . \quad . \quad . \quad (6)$$

The kinetic energy of the electron is $\frac{1}{2}mV^2$, or, from (3):

$$\text{Kinetic energy} = \tfrac{1}{2}m(2\pi\omega r)^2 = \frac{1}{2} \cdot \frac{eE}{r} \quad . \quad . \quad . \quad (7)$$

In a system consisting of electrons and a positive nucleus, in which the nucleus is at rest, and the electrons move in circular orbits with a velocity small in comparison with that of light, the kinetic energy is numerically equal to half the potential energy (*cf.* 1. 13, 14). The work, W, required to move the electron from its orbit to a position of rest at infinity is the difference between the potential and kinetic energies of (5) and (6), or $\frac{1}{2}eE/r$. Therefore, the potential energy, W, of an electron in its orbit is:

$$W = \frac{eE}{2r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where W may have any value ranging from zero to infinity.

It is assumed that the electron does not radiate any energy while it is smoothly revolving about the nucleus, for if energy were continuously dissipated by radiation, the loss would go on increasing so that the radius, r, would continually decrease and the frequency, ω, increase. Otherwise expressed, the orbit would get smaller, and the motion would increase until finally the electron would fall into the nucleus. The spectrum emitted by such a system would thus change continuously. N. Bohr, therefore, introduced an assumption to prevent this continuous change. He postulated that the steady states of motion are those, and only those, for which the energy, W, changes by an exact multiple of the universal constant, such that, *i.e.*

$$W=\tfrac{1}{2}nh\omega \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where n is a positive integer. This conception, originally due to J. W. Nicholson, is equivalent to assuming that energy is atomic, and changes only in multiples of $\frac{1}{2}h\omega$; which may be regarded as a unit, or an atom of energy. Another interpretation is that the angular momentum, $2\pi m\omega r^2=\frac{1}{2}nh/\pi$, so that in any molecular system consisting of positive nuclei and electrons in which the nuclei are at rest relative to each other, and the electrons move in circular orbits, with a velocity which is small in comparison with that of light, the angular momentum of every electron round the centre of its orbit will, for the permanent state of the system, be equal to $h/2\pi$, where h is Planck's constant. Other interpretations of this assumption have been given. From (6), (8), and (9), it follows that of all circular orbits only those are stationary whose radii are

$$r=\frac{h^2n^2}{4\pi^2meE} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where n is 1, 2, 3. . . . Since the smallest of these quanta-radii is that for which $n=1$, introducing, in C.G.S. units, the values $e=4{\cdot}7\times10^{-10}$; $e/m=5{\cdot}3\times10^{17}$; or $m=0{\cdot}9\times10^{-27}$; and $h=6{\cdot}5\times10^{-27}$ obtained from other independent observations; and putting, for hydrogen, $E=e$, it follows that r is $0{\cdot}6\times10^{-8}$ cms., which is the right order of magnitude. It is, however, an essential part of the theory that there can be hydrogen atoms n^2 times this size, where $n=2$, 3, 4, . . . Again, from (8) and (10), the value of the energy, W, is

$$W=\frac{2\pi^2me^2E^2}{n^2h^2} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

For hydrogen, $n=1$, and $e=E$; therefore, $W=2\pi e^4m/h^2$, or $2{\cdot}0\times10^{-11}$; and for the ionizing potential, $W/e=0{\cdot}043$, which corresponds to 13 volts—J. J. Thomson gave 11 volts.

So long as the atom is left to itself the electron will move in one of the orbits :

$$W=\frac{2\pi^2me^2E^2}{n^2h^2}$$

without emitting any radiation ; but if through some external agent—say, exposure to cathode rays—the electron, by some unknown mechanism, is thrown from its stationary orbit, n_1, into another orbit, n_2, at the same time, the energy changes from W_1 to W_2 ; and with the shrinkage of orbits, the system suffers a loss of energy :

$$\delta W=W_2-W_1=\frac{2\pi^2me^2E^2}{h^2}\left(\frac{1}{n_2{}^2}-\frac{1}{n_1{}^2}\right) \quad . \quad . \quad . \quad (12)$$

The shrinkage is assumed to be attended by the loss of the whole of the energy, which is radiated into space in the form of monochromatic radiation of frequency, ν. N. Bohr further assumes that the amount of this loss is just one quantum, ϵ (*vide* **1.** 13, 15). Hence, $\delta W=h\nu$, or, from (12) :

$$\nu=N\left(\frac{1}{n_2{}^2}-\frac{1}{n_1{}^2}\right) \quad . \quad . \quad . \quad . \quad (13)$$

where $N=2\pi^2me^2E^2/h^3$. As before, substituting, for hydrogen, the known values of the different terms, it follows that $N=3{\cdot}26\times10^{15}$; this agrees closely with the observed value, $3{\cdot}290\times10^{15}$. The frequency, ν, is the reciprocal of the period of the emitted waves, and in experimental work it is usual to quote the reciprocal λ^{-1} of the wave-length in vacuo. If V_∞ denotes the velocity of light in vacuo, $\lambda^{-1}=\nu/V_\infty$, and $\lambda^{-1}=N'(n_2{}^{-2}-n_1{}^{-2})$, where $N'=N/V_\infty$, the so-called *Rydberg's constant ;* putting $V_\infty=3\times10^{10}$ cms. per sec., it follows that $N'=1{\cdot}005\times10^5$, in close agreement with the observed value 109,675—all in C.G.S. units.

It is here assumed that the mass of the nucleus, M, is very great in comparison with m, the mass of the electron. If the ratio m/M be not negligibly small, m must be replaced by $mM/(M+m)$, and the value of Rydberg's constant is reduced by the factor $M(M+m)$. For hydrogen $N \times 109{,}675$ agrees very well with observation, for helium, the corrected value $N'=NM/(M+m)$. A. Fowler found that the hydrogen lines observed by him were not accurately represented by formula (13). N. Bohr, however, showed that this objection does not apply if the mass of the central nucleus be taken into account by making $N'=NM/(M+m)$. This also agrees with the observations of E. J. Evans. The ratio $m/M=1:1836$ very nearly.

The neutral hydrogen atom is assumed to have one electron, Fig. 4, and hence $E=e$. If the atom acquires another electron, as it does in the canal rays, it will be negatively charged, Fig. 5. The relative sizes of the neutral and negatively charged atoms are illustrated by the diagrams, Figs. 4 and 5.

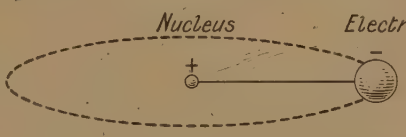

Fig. 4.—Neutral Hydrogen Atom (Diagrammatic).

E. Rutherford proposed to apply the term *proton* to the hydrogen nucleus of mass one, and unit positive charge; O. Masson suggested the term *baron*. O. J. Lodge has suggested a number of terms but preferred *hylon*; A. H. Patterson, *hydron*; F. Soddy said that the term *hydrion* is already in use for the positively charged hydrogen ion. A. H. Compton has also discussed this subject.

Since the configuration with the neutral hydrogen, Fig. 4, has a greater value for W than the configuration with the negatively charged hydrogen atom, Fig. 5, it might be anticipated that a hydrogen atom can under certain conditions acquire a negative charge; but since the energy of a hydrogen atom with two negative charges is very small, a hydrogen atom cannot be expected to acquire two negative charges.

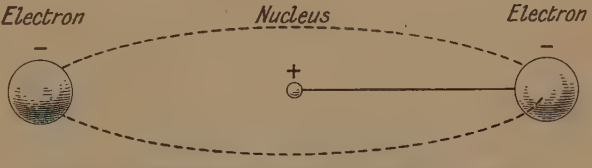

Fig. 5.—Negatively Charged Hydrogen Atom.

If the integral constant, n_2, in (7) be made unity, and n_1 be assigned integral values greater than n_2, say, $n=2, 3, 4, \ldots$, a series of spectral lines is obtained. These lie in the ultra-violet. This series was not known when N. Bohr published his theory, but has since been discovered by T. Lyman—*Lyman's series*. If n_2 be assigned the value 2, and n_1 be made 3, 4, 5, . . ., the well-known *Balmer's series* (1. 7, 7) is obtained. If n_2 be assigned the value 3, and n_1 be made 4, 5, 6, . . ., *Paschen's series* in the infra-red is obtained. Higher

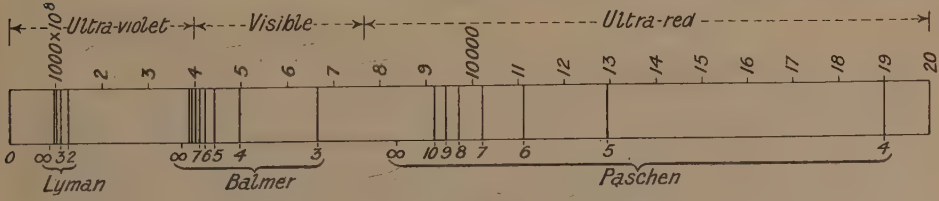

Fig. 6.—The Series Spectra of Hydrogen.

values of n_2 are too far in the infra-red to be observed. These series are illustrated diagrammatically by Fig. 6. The Balmer series has not been observed in the laboratory beyond the line $n_1=12$, but in stellar spectra, the series has been followed to $n_1=33$. It is assumed that in vacuum tubes, there are no hydrogen atoms of greater diameter than that given by $n_1=12$, where the calculated radius $r=0{\cdot}8\times10^{-6}$ cms., which is equal to the mean distance in the mols. of the gas at

about 7 mm. press.; but for $n_1=33$, the radius is $r=0{\cdot}6\times10^{-5}$ cms., and the press. about 0·02 mm. On this theory, therefore, there may be hydrogen atoms in the stars about a thousand times greater than the size of the normal atom.

The formation of a molecule of hydrogen from two atoms of that element is considered by N. Bohr. The nuclei of two such atoms repel one another. If the electrons of two adjacent atoms are rotating in the same direction, two parallel currents of electricity are in proximity, and therefore attract one another, and arrive in the same plane. The molecule thus consists of the electrons which revolve like the governor-balls of an engine about an axis formed by the two nuclei. He calculated the energy liberated in the process of combination $2H=H_2$ to be 60 Cals. per mol, a result in substantial agreement with the value 76 Cals. per mol, calculated by I. Langmuir from the heat conduction of an incandescent wire in hydrogen. The last-named first gave 130 Cals., but, after N. Bohr's calculation, he revised the calculation and reduced 130 to 76 cals.

According to N. Bohr, the neutral helium atom has two electrons revolving about the nucleus, Fig. 7, so that the nuclear charge is $E=2e$. When from ionization, or other cause, the atom loses one electron, the remaining positively charged atom has one electron, with charge $e=\frac{1}{2}E$, revolving about the nucleus. The spectral lines are accordingly represented by putting $E=2e$, and, from (13), the frequency will be given by $\nu=4N(n_2^2-n_1^2)$. The series with $n_2=1$ and $n_2=2$ are too far in the

Fig. 7.—Neutral Helium Atom.

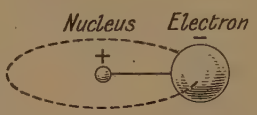

Fig. 8.—Positively Charged Helium Atom.

ultra-violet to be observed; but the series $n_2=3$ can be divided into two parts according as n_1 is odd or even; and both series have been observed by A. Fowler with mixtures of hydrogen and helium, when the hydrogen seems to be required to ionize the helium. At first the spectrum was attributed to hydrogen, but they are now regarded as being produced by positively charged helium atoms. Similarly, when $n_2=4$, the spectrum consists of two parts, according as n is even or odd. If even, a series analogous to J J. Balmer's series is obtained, the so-called *W. H. Pickering's series*. The latter series was observed in 1896 in the spectrum of the star ζ-Puppis, and attributed to hydrogen.

N. Bohr applied his theory to the lithium atom on the assumption that the atom has three electrons; the nuclear charge is $E=3e$. This atom should give the spectral series $\nu=9N(n_2^{-2}-n_1^{-2})$, and in the special case for $n_2=2$, in addition to the lines coinciding with J. J. Balmer's series, J. W. Nicholson observed a pair of series with $n_1^2=(m\pm\frac{1}{3})^2$, in the spectra of the Wolf-Rayet stars.

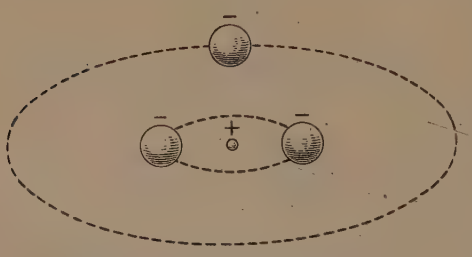

Fig. 9.—Neutral Lithium Atom.

N. Bohr's theory does not account for the ordinary spectrum of hydrogen or helium. J. W. Nicholson has shown that coplanar, concentric rings of vibrating electrons are unstable when electrostatic forces are alone taken into consideration; but N. Bohr maintains that no such oscillations occur in the plane of the orbit of the electrons, and the objection does not apply. J. W. Nicholson bases his calculations on an atom of the Rutherford type, but he does not use the quantum hypothesis. The energy which is required to produce the spectrum comes from outside, and is

not, as in N. Bohr's theory, atomic energy. Two elements have been recognized by their spectra, but they have not yet been recognized on earth—*coronium* occurs in the coronal spectrum of the sun; and *nebulium* in the spectra of nebulæ. He calculated the possible spectral lines of nebulium, and found that the theory did not account for two of the lines which had been recorded for this element in the spectra of the nebulæ. M. Wolf later found that these two lines in the spectrum of the ring nebula in Lyra had a different origin from the true nebulium lines; J. W. Nicholson also predicted the existence of a new nebulium line not previously noticed, which W. H. Wright found on photographic plates taken years previously, but which was so faint that it escaped notice.

Working from an atom of the Rutherford type, J. W. Nicholson (1914) has calculated spectral lines for vibrating electrons in systems with an assumed atomic number 1*e*, 2*e*, 3*e*, 4*e*, 5*e*, and 6*e*, and with the respective at. wt.:

Element	Prh	—	—	Nu	Pf	Arc
At. number	1*e*	2*e*	3*e*	4*e*	5*e*	6*e*
At. wt.	0·082	0·327	0·736	1·31	2·1	2·9

The lines corresponding with 1*e* exist in the spectra of nebulæ and have been assumed to belong to an unknown primitive element called *proto-hydrogen*, Prh; the lines corresponding with 2*e* are present in nebulæ and in Nova Persei; similarly faint lines corresponding with those computed for 3*e* are found in nebulæ; 4*e* belongs to *nebulium*, Nu; the lines for 5*e* have not been found in nebulæ, but those in the solar corona have been supposed to represent a non-terrestrial *proto-fluorine*, Pf; the lines for 6*e* exist in the spectra of nebulæ and have been supposed to represent an unknown element *arconium*, Arc. Lines corresponding with 7*e* are also found in nebulæ.

According to F. A. Lindemann, N. Bohr's is but one of a number of models which can be devised to explain the structure of the atom from the standpoint of mechanics. The possible models may be grouped as static or dynamic. In each case assumptions must be made to assure the stability of the atom. Chemists prefer to consider the valency electrons as fixed on the surface of the atom in certain definite positions; this coincides with numerous observations such as the existence of the asymmetric carbon atom, the phenomena of stereochemical hindrance, etc. If a statical model be assumed, with the valency electrons in definite positions in the atoms, and a central positive nucleus, it is necessary to assume repulsive forces in the atom which act in opposition to the attractive forces between positive and negative charges. Thus, J. J. Thomson said that there is no necessity to assume that the observed laws of electrostatics prevail at very small distances. He postulated that the forces acting on an electron in an atom are (i) a radial repulsive force varying as the cube of the distance from the centre, and diffused uniformly through the whole atom; and (ii) a radial attractive force varying inversely as the square of the distance from the centre, and confined to a limited number of radial tubes of force in the atom. By this means he is able to explain the relation between the velocity of emission of the electrons and the incident frequency; and to explain Balmer's series. W. Peddie also explained the variation in the properties of atoms and molecules as due to structural conditions within the atom, and to the presence of regions of attractive force alternating with regions of repulsive force. J. J. Thomson favoured a statical theory; he said in respect to N. Bohr's theory:

> It seems hardly likely that much progress can be made in the soln. of the difficult problems relating to chemical combination by assigning in advance definite laws of force between the positive and negative constituents of an atom, and then on the basis of these laws building up mechanical models of the atom. We must first af all, from a study of chemical phenomena, learn the structure and arrangement of the atoms, and if we find it necessary to alter the law of force acting between charged particles at small distances, even to the extent of changing the sign of that force, it will not be the first time in the history of science that an increase in the range of observational material has required a modification of generalizations based upon a smaller field of observations. Indeed in the present

case, entirely aside from any chemical reasons, a study of the mathematica theory of the electrons leads, I believe, irresistibly to the conclusion that Coulomb's law of inverse squares must fail at small distances.

In the dynamical models, favoured by N. Bohr, J. W. Nicholson, etc., the chemical facts are not so much emphasized, the repulsive force is replaced by a centrifugal force, and it is assumed that the electrons in rotation do not radiate energy. The mathematical treatment is largely concerned in finding whether an assumed configuration of electrons and nucleus will be stable mechanically; the chemical properties appear to be of secondary importance. The case for the ring electron has been summarized by H. S. Allen; on the physical side it has been adapted to explain: (i) the loss of energy by radiation; (ii) diamagnetism and paramagnetism; (iii) the asymmetry of certain types of radiation; (iv) the absorption of X-rays by magnetic substances; (v) the ionization of gases by X-rays; (vi) thermoelectric effects; (vii) the radiation formula of M. Planck; (viii) series lines on spectra; (ix) the Zeeman effect; (x) the Stark effect; (xi) solar electron streams and auroræ; (xii) cohesion; etc.

The periodic law.— Ever since J. B. A. Dumas (1851) wrote:

> Every chemical compound forms a complete whole. Its chemical nature depends primarily on the arrangement and number of the constituent atoms, and to a less degree on their chemical nature,

it has been considered a fundamental principle in chemistry that substances similarly constituted have similar properties. If stable aggregates of electrons are similarly constituted, the properties of the resulting atoms, within certain limitations, will be similar even though the at. wt. be different. In W. Kossel's modification of J. J. Thomson's ring system, the two- and eight-ring systems are assumed to be the most stable, and while the outer ring of electrons determines the valency of the atom, the inner stable rings determine the characteristic properties of the element. The first series in the periodic table has an inner ring with two electrons and an outer ring with from zero to seven electrons, the addition of one more electron to the outer ring makes a stable ring from which no more electrons can escape:

First series .	(2)	(2)1	(2)2	(2)3	(2)4	(2)5	(2)6	(2)7
Second series .	(2,8)	(2,8)1	(2,8)2	(2,8)3	(2,8)4	(2,8)5	(2,8)6	(2,8)7
Third series .	(2,8,8)	(2,8,8)1	(2,8,8)2	(2,8,8)3	(2,8,8)4	(2,8,8)5	(2,8,8)6	(2,8,8)7

Hence, when the elements are arranged in the order of increasing mass, there is a certain similarity in the grouping at certain intervals. Thus, the properties connected with a two-ring group can only recur at intervals; similarly with more complete systems. Consequenly, we can divide the various groups of electrons into families such that any one family is derived from the preceding members by the addition of another ring of eight electrons. This idea gives a rather definite conception of the meaning of the periodic law. A periodic law thus appears as a necessary consequence of the hypothesis that atoms are built of stable systems of concentric rings of electrons; for obviously, without specifying particular numbers, *certain rings of electrons recur periodically with an increase in the number of electrons which make up the atom*, and atoms with related rings must possess many common properties in virtue of the similarity in the grouping of some of the rings. Thus, J. J. Thomson has demonstrated that the spectra of such groups would be in many ways similar.

It is even possible to see how elements with similar properties may fall into the "wrong" group in Mendeléeff's table if classed solely by their at. wt. Starting from sodium in the periodic table, it follows that if the atoms of the elements are really aggregates of electrons, the sodium atom might collect more electrons until, say, two different stable systems capable of separate existence are formed. Thus, sodium might furnish two subgroups—potassium and copper. The properties of an element are supposed to be determined by the structure of rings of electrons,

and differences in the properties of members of the subgroups is due to the differences in the internal structure of the atoms although the atoms probably possess some rings in common. Each subgroup, by a further condensation of electrons, forms the succeeding family members indicated in the vertical columns of the table. Consequently, it is quite true, in a general way, to say that the elements were evolved in the order of their at. wt., but they must also have evolved in groups down the vertical as well as along the horizontal lines of Mendeléeff's table. Hence, as J. N. Lockyer observed, the elements do not always appear in the cooling stars in the order of their at. wt. In virtue of this **multiple growth hypothesis** of A. C. and A. E. Jessup, it is to be expected that in some cases an element in any particular group may contain more or less electrons, and hence have a slightly greater or less at. wt. than adjacent elements in the next succeeding group.

Again, since the nuclear charge of an atom of any element corresponds to the position of the element in the series of increasing at. wt., and since the physical and chemical properties of an element depend on the magnitude of this nuclear number; and since any given number of electrons may conceivably assume different stable configurations, it is possible for two or more elements to have the same nuclear charge, and to occupy the same place in the periodic table. These are the isotopes or isotopic elements of F. Soddy and co-workers.

The mechanism of multi-electronic systems has not been followed so far as in the simple case of hydrogen. It is, however, assumed that the electrons are arranged in rings about the nucleus, but the number and orientation of the rings is unknown. In the absence of more definite information, the *periodic law* is taken to indicate that the disposition of the electronic rings, with elements of low at. wt. arranged according to their atomic number, is such that, with a periodicity of 8, every 9th element is similar to the first. This is illustrated in Table III. Again, the valency of a series of eight elements rises from zero to four, and then decreases back to zero. The valency of an element is taken to be fixed by the number of electrons in the outermost ring, and it is through the agency of these electrons that one atom is coupled to another. With elements of low at. wt., the number of electrons in the outermost ring will be odd or even according as the total number of electrons in the atom is odd or even. This means that the valency of an element of low at. wt. is odd or even according as the at. number of the element in the periodic series is odd or even. The binding of the outer electrons in any horizontal series will become weaker with increasing electrons per atom. This corresponds with the observed increase in the electropositive character of an element for an increase of at. wt. in any group of the periodic system. At. vols. are usually deduced from measurements on molecules *en masse*, and it is observed that the elements in the same column of the periodic system have approximately the same at. vol., while the volume changes from column to column and is greatest for columns corresponding with the smallest valency and smallest for elements with a valency of 4. The number of electrons in an atom is taken to be fixed by the at. number of the element. Both A. van den Broek, and N. Bohr state that the at. number is equal to the number of positive charges on the nucleus such that the positive charges are numerically equal to Ne. J. Chadwick found that when measured at any point between 3×10^{-12} and 10^{-10} cms. from the nucleus, the nuclear charge is equal to the at. number; and the law of force is that of the inverse square. It is also inferred that there are no electrons between the nucleus and the ring K-radiation electrons. F. Sanford calculated the magnitude for the central positive charge of an atom from the equation for the orbital motion and the equation $\frac{1}{2}MV^2=h\nu$; but the latter requires h replacing by a function of mass, m. C. G. Barkla regarded the charge on the nucleus to be $\frac{1}{2}Ae$, where A is the at. wt. of the element. The first two electrons are taken to be arranged in a single ring; and the next two electrons in another ring. A ring with four electrons will have a smaller value for the total energy than two rings with two electrons in each. It is assumed that a ring with four electrons will not occur before boron, at. number 5, or carbon, at. number 6, on account of the observed ter-

or quadri-valency of these elements. The periodic system suggests that in neon, at. number 10, a ring of eight electrons occurs ; and unless the at. number is greater than 13, the configuration with two rings each with four electrons will correspond to a smaller value for the total energy than a configuration of one ring with eight electrons. N. Bohr's arrangement of the electrons in the atoms of elements of low at. wt.—from hydrogen to chromium—is shown in Table III. The iron-group occurs

TABLE III.—N. BOHR'S ARRANGEMENT OF ELECTRONS IN THE ATOMS OF ELEMENTS OF LOW ATOMIC WEIGHT.

Atomic number.	Element.	1st ring.	2nd ring.	3rd ring.	4th ring.	5th ring.
1	Hydrogen	1	—	—	—	—
2	Helium	2	—	—	—	—
3	Lithium	2	1	—	—	—
4	Beryllium	2	2	—	—	—
5	Boron	2	3	—	—	—
6	Carbon	2	4	—	—	—
7	Nitrogen	4	3	—	—	—
8	Oxygen	4	2	2	—	—
9	Fluorine	4	4	1	—	—
10	Neon	8	2	—	—	—
11	Sodium	8	2	1	—	—
12	Magnesium	8	2	2	—	—
13	Aluminium	8	2	3	—	—
14	Silicon	8	2	4	—	—
15	Phosphorus	8	4	3	—	—
16	Sulphur	8	4	2	2	—
17	Chlorine	8	4	4	1	—
18	Argon	8	8	2	—	—
19	Potassium	8	8	2	1	—
20	Calcium	8	8	2	2	—
21	Scandium	8	8	2	3	—
22	Titanium	8	8	2	4	—
23	Vanadium	8	8	4	3	—
24	Chromium	8	8	4	2	2

at the end of the third period of eight elements. Here the elements of neighbouring groups show similar chemical properties, indicating that the configurations of the electrons in the elements of this group differ only in the arrangement of the inner electrons. After the iron group, the period is no longer 8 but 18, suggesting that the elements of higher at. wt. have a recurrent configuration of 18 electrons in the innermost ring. Such a ring would probably be unstable, and the electrons may be arranged in two parallel rings. The presence of the rare earth group indicates that an alteration of the innermost rings occurs.

In the case of **multivalent elements,** it is possible that electrons can move from the outer to an inner ring, so that multivalency corresponds with a kind of infra-atomic tautomerism. Thus, with univalent copper, the arrangement for the atoms would be 2, 8, 8, 10, 1, while with bivalent copper the arrangement may be 2, 8, 8, 9, 2.

Line spectra.—If through some agency like electronic bombardment, one or more electrons in the ring *B* of a neutral atom of, say, calcium, Fig. 10, be made to revolve in the ring *C*, the displaced electron would not radiate while moving in the orbit *C*, but it would send out a radiation of a single definite wave-length in passing back from *C* to the stable orbit *B*. If the disturbance cause one or more electrons in orbit *B* to revolve in orbit *D*, then as the electrons dropped back either directly to orbit *B*, or to orbit *C* first and then to *B*, the atoms in returning to the neutral

state might emit a radiation of two or possibly three definite and determinate wavelengths. Atoms may thus emit a 1, 2, 3, . . . line spectrum according to the violence of the shock to which they are subjected.

Single line spectra are attributed to oscillations produced by the return to their orbits of electrons which have been displaced by some external influence. J. C. McLennan and J. P. Henderson found that the vapours of cadmium, zinc, and mercury emit single line spectra when traversed by electrons possessing the proper amount of energy. Spectra with lines are obtained with voltages 15·3, 11·85, and 12·5 respectively; below the voltages there is a definite range for each metal in which the characteristic single line spectra alone can be excited. In the simple case, the single line spectrum may be produced by the return of the electron, and in the case of spectra with many lines, by the return of a complete ring of electrons to their original positions about the central nucleus. J. C. McLennan also obtained similar results with magnesium. J. C. McLennan and J. P. Henderson obtained the following potentials in volts representing the work required to remove an electron from a neutral molecule:

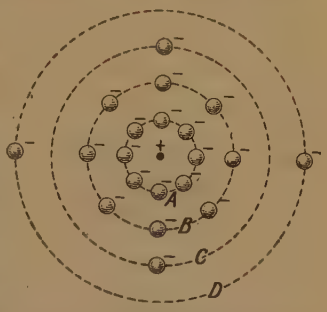

FIG. 10.—Electrons in Bohr's Atoms of Calcium.

Mg	Zn	Cd	Ca	Sr	Ba	Li	Na	K	Rb	Cs
4·28	4·04	3·81	2·94	2·69	2·24	1·85	2·11	1·61	1·56	1·39

J. Franck and H. Hertz obtained 4·9 volts for the ionizing potential of mercury, and with electrons of such a voltage, mercury vapour emits a single line spectrum $\lambda=2537$. This amount of energy corresponds very nearly with a quantum of energy $h\nu$, where ν is the frequency of the observed spectrum line. If e denotes the charge in the electron, the relation between volts, V, and frequency ν is $Ve=h\nu$. The order in the above table agrees with the known electropositive characters of the different elements. It also shows that some atoms have a greater affinity for electrons than others; the atoms with the lowest electron affinity belong to the elements characterized as electropositive.

W. Kossel assumes that the K-radiation occurs when an electron jumps from the third ring to take the place of one removed from the first or innermost ring, L-radiation corresponds with the removal of an electron from the second ring, and M-radiation, with the removal of an electron from the third ring. W. Kossel then infers that there are as many lines in these high-frequency spectra as there are rings in the atom; and the frequencies of the different lines are related as

$$\nu_{K\beta}-\nu_{K\alpha}=\nu_{L\alpha};\ \text{and}\ \nu_{K\gamma}-\nu_{K\beta}=\nu_{L\beta}-\nu_{L\alpha}=\nu_{M\alpha}$$

where the subscripts refer to the lines in each series. He showed that these relations are satisfied by the elements ranging from calcium to zinc. I. Malmer also found the K_α- and K_β-lines of some elements of higher at. wt. are in accord with W. Kossel's rules.

The absorption spectrum of a gas can be readily interpreted on N. Bohr's theory, for if in an inert gas the majority of the atoms are in the state $n=1$, and radiation passes through the gas in complete quanta, a quantum can be absorbed only if it is adequate to move an electron from one orbit to another, or to set the electron free altogether. Thus the absorption spectrum will consist of the series $n_2=1$ together with a continuous absorption band running upwards from the head of this series, where $n_1=\infty$. The range covered by this band is the range for which the photoelectric effect occurs, and the presence of this absorption band is evidence of the occurrence of photoelectric action. According to R. W. Wood, the absorption spectrum of *sodium* vapour is of this type. Fifty lines were observed in the absorption spectrum, and their position agreed with those of the principal sodium series, and in

addition, there was a continuous absorption band beginning at the head of this series, and extending to the ultra-violet.

According to N. Bohr, the hydrogen atomic system with a circular orbit has one degree of freedom, but A. Sommerfeld showed that more probably the atomic system has two degrees of freedom, and that the electrons may move in elliptical orbits of every eccentricity in one place. A. Sommerfeld's calculations also show that a single line in the spectrum does not correspond necessarily with the passage from one possible state to another possible state, but rather from one group of possible states to another group of such states. He thus extended N. Bohr's theory to explain the fine structure of hydrogen and similar series lines, and the X-ray spectra. Some spectral lines, even in the absence of magnetic or electric fields, are not strictly single, but have a number of satellites. It may be that this separation is due to some perturbation which distorts the elliptical orbits making the energies of ellipses of different eccentricities not the same. A. Sommerfeld says there is no perturbation; he has shown that it has been assumed that the mass, m, of the particles is independent of their velocity; and in place of m he substitutes H. G. Lorentz's expression, $m=m_0(1-\beta)^{-\frac{1}{2}}$—*vide supra*—and obtained some results which agree with observation.

The subject has been further discussed by M. Siegbahn, P. Ehrenfest, L. Föppl, T. Rella, O. Hinsberg, F. Reiche, A. Rubinowicz, S. R. Milner, E. Gehrcke, F. Kirchhoff, R. T. Birge, T. Terada, J. Larmor, H. S. Allen, O. Chwolson, E. C. Kemble, L. Vegard, M. Brillouin, R. Ladenburg, A. Smekal, J. Franck and F. Reiche, J. Franck and W. Grotrian, J. Stark, E. O. Hulburt, W. H. Westphal, A. Szarvassi, H. T. Wolff, A. Landé, P. Debye, R. Glocker and M. Kaupp, J. Kroo, F. Wenzel, E. Kohlweiler, A. Berthoud, K. Fehrle, J. Chadwick, R. Ladenburg, G. A. Schott, N. Nordström, G. Laski, G. Kirsch, F. J. Wisniewsky, W. D. Harkins, S. H. C. Briggs, F. A. Henglein, A. E. Lacomblé, S. N. Basu, K. Fösterling, H. Teudt, J. Marshall, M. and L. de Broglie, A. Korn, W. Schottky, J. M. Burgers, W. Kossel, G. H. Darwin, A. C. Crehore, O. J. Lodge, H. A. Wilson, W. Daune, W. Heisenberg, A. D. Fokker, M. C. Neuburger, H. S. King, M. Yamada, L. Meitner, M. Brillouin, W. M. Hicks, J. C. McLennan and P. Lowe, O. Oldenberg, E. T. Whittaker, J. A. Ewing, W. Peddie, R. A. Houstoun, J. Duclaux, J. S. Townsend and V. A. Bailey, etc. L. Silberstein applied the theory to atomic systems containing a complex nucleus. A. Smekal discussed the action of the electronic rings in the atom; P. Ehrnfest and N. Bohr, the spectral lines of isotopes.

W. D. Harkins and E. D. Wilson showed that the at. wt. of the elements with low at. wt., beginning with helium, are not multiples of the at. wt. of hydrogen by a whole number; but the multiple differs from a whole number by a nearly constant percentage difference—average −0·77 per cent. They call this the *packing effect*, and regard it as the percentage decrease of mass when hydrogen atoms are aggregated to form more complex atoms. They also developed a scheme of which the atoms of the elements could be regarded as complexes of hydrogen or helium nuclei.

Null-valency.—As just indicated in W. Kossel's ring system, modified from that of J. J. Thomson, it is assumed that the two- and eight-ring systems are the most stable. Such rings are not readily broken down. If an electron escapes from such a system, the positively charged residue will attract surrounding electrons, so that one will immediately dart back to it, and reform the original system. The system so formed will break up as before, and the same cycle of changes would be repeated over and over again. Hence the system will not remain permanently charged; directly it loses an electron another takes its place. Such an atom will be unable to retain a positive or negative charge permanently; and it will not be able to enter into chemical combination. Consequently, it will behave like the members of the group of inert gases.

Electronegative and electropositive characters.—The majority of those working on the structure of the atom believe that the outer ring of the electrons determines the periodicity and valency of the atoms of the elements. C. A. Kraus argues as follows: The outer electrons are held loosely and are able to move from atom to atom. These electrons are very sensitive to changes in condition, such as temp., press., the presence of other atoms, etc. So weak is the bond connecting the electron to an atom, that more electronegative atoms may remove it from the

original atom in question. *The less tendency the metal has to retain its electron, the more electropositive it becomes, and the more readily does it in general react chemically.* Ordinarily, the positive and negative constituents of a compound are held together through the medium of the electron. Under certain conditions, however, the electrostatic force acting between the metallic atom and its electron becomes weakened to such an extent that the negative constituent escapes, carrying the electron with it. The same result may be obtained at high temp. with the fused salt or even with the solid compound. That is when sodium and chlorine combine, the sodium atom gives up an electron to the atom of chlorine, and the atoms are thus held together by the electrostatic forces between the positively charged residue of the sodium atom and the negatively charged atom of chlorine. In a soln. of high dielectric constant such as water, these electrostatic forces are weakened to such an extent that **ionization** occurs resulting in the formation of $Na^{\cdot}$ and Cl' ions. Naturally the properties of those ions are radically different from those of metallic Na and gaseous Cl_2 as we know them. Consider the properties of the systems with a 2-electron ring on the inside, supposed, in W. Kossel's system, to be

Li	Be	B	C	N	O	F
(2)1	(2)2	(2)3	(2)4	(2)5	(2)6	(2)7

When the first member with three electrons is subjected to a small disturbance, an electron is detached from the outer ring. When one electron is lost, the residue has a positive charge, and behaves like a positively charged ion, that is like an electropositive or basic element. The system with four electrons is more stable than the one with three, and it will not be so readily broken as the preceding. This means that this system will not be so basic as the preceding. Similarly the system with five electrons will be less basic than the one with four; and six will be less basic again than five. In the six-electron system the stability is so great that there is little danger of losing electrons from the outer ring, and an electron could lie on the surface of the system without breaking a ring. In that case, the system would receive a negative charge and behave like an electronegative or acidic element. Hence, **the electronegative elements may be regarded as possessing neutral atoms with a tendency to absorb negative electrons from without, and electropositive elements are regarded as neutral atoms with a tendency to part with negative electrons.** The electronegative character increases with increasing at. wt. until the system with nine electrons is reached. This corresponds with the fact that in Mendeléeff's list of elements the electronegative property is practically zero at the end with the alkali metals, and gradually becomes more marked with increasing at. wt. until, at the halogen end, it attains its maximum value. The system with ten electrons resembles the one with three in respect to stability, etc., and the system with eleven resembles the one with four, and so on. The system of three electrons will be most electropositive of the series, with two electrons in the inner ring. It can lose but one electron because, if it lost two, the residue with one electron would immediately attract an electron. Hence, the three-electron system can lose one electron and form a system carrying unit charge of positive electricity. This means that such a system is univalent. The four-electron system would not be so ready to part with electrons as the three-electron system, but it could afford to lose two electrons since it is not reduced to the unstable one-electron group until it has lost three electrons. The group with four-electrons must therefore be bivalent. Against this, however, it must be remembered that positive ray analysis shows that there is no relation between the number of electrons an atom can lose and the valency of the element; thus the inert gas helium readily loses two electrons; the argon atom can carry one, two, or three positive charges; krypton, four; etc.

Chemical combination.—Suppose that we have an atom of the type (2,8)1, and one of the type (2,8)7; the former would be illustrated by an atom of sodium, and the latter by an atom of chlorine: the former can *lose* one negative electron, and the latter can *gain* one, but not more than one. The electrons which escape

from the sodium atom can find a home on the chlorine atom, and if an eq. number of both be present, each of the sodium atoms will acquire a positive charge, and each of the chlorine atoms a negative charge. The oppositely electrified atoms will attract one another, and form a compound NaCl. When electropositive and electronegative atoms are brought into proximity, the former loses and the latter gains an electron, as a result, the former acquires a positive and the latter a negative charge; and **the force of chemical affinity is the attraction exerted by the electropositive atom for the electron it has lost to the electronegative atom.** Similarly, if eq. quantities of atoms of the type (2,8)2 and (2,8)7 were to be mixed together, and this would be illustrated by magnesium and chlorine atoms, the atoms of magnesium would each lose two negative charges, and each of the chlorine atoms would gain one negative charge. Thus a neutral system would be formed by the combination of two chlorine atoms with one magnesium atom, and $MgCl_2$ would result. Hence, says J. J. Thomson, from this point of view a univalent electropositive atom is one which can lose one and only one electron to form a stable system under conditions which prevail when chemical combination is taking place. Similarly, *mutatis mutandis*, with univalent electronegative atoms, bivalent atoms, etc. Thus, **the affinity of an atom depends upon the ease with which an electron can escape from or be received by the atom.** This may be influenced by the conditions prevailing at the time chemical combination is taking place. If the atoms be diffused in a good conducting medium it would be easier for a liberated electron to resist being pulled back to the original atom than if the atoms were diffused in a non-conducting medium. Hence, the valency of an atom may be influenced by the physical conditions under which it is placed. **The ability of an atom to enter into chemical combination depends upon its power of acquiring a charge of electricity.** Thus chemical affinity is electrical affinity, or, as H. Davy expressed it in 1810, " electrical and chemical attractions are produced by the same cause acting in one case on particles, and in the other on masses."

Abegg's normal and contra-valencies.—We have just seen that the (2,8)1-system can acquire one and only one positive charge by the loss of one negative electron; but it is conceivable that additional negative electrons could be forced into the system so that the total number of electrons increase to (2,8)2, (2,8)3, (2,8)4, . . . (2,8)7; and at the same time the systems would become more and more stable. If an additional electron were forced into the (2,8)7-system, a system with (2,8)8 electrons would be formed. Consequently, (2,8)7 is the greatest number of negative electrons which we can hope to force into the (2,8)-system to furnish a stable system with an electronegative valency of 7—the electropositive valency of the (2,8)1-system is one. Similarly, *mutatis mutandis*, with the other systems, and the properties of the systems containing (2,8)1 to (2,8)7 electrons can be tabulated as follows:

Number of electrons	(2,8)	(2,8)1	(2,8)2	(2,8)3	(2,8)4	(2,8)5	(2,8)6	(2,8)7	(2,8)8
Valency	+0	+1	+2	+3	+4	−3	−2	−1	−0
	−8	−7	−6	−5	−4	+5	+6	+7	+8
	Electropositive.					Electronegative.			

This sequence of properties imitates that observed with the elements:

He, Li, Be, B, C, N, O, F, Ne
Ne, Na, Mg, Al, Si, P, S, Cl, A

The first and last members of the series only are null-valent; the second set is univalent electropositive, and the last but one univalent electronegative; the third is bivalent electropositive, and the last but two bivalent electronegative, etc.

This recalls an observation of D. I. Mendeléeff to the effect that the sum of the maximum oxygen and hydrogen valencies of the elements in certain groups of the periodic series is equal to 8; *e.g.*,

SiH_4	PH_3	SH_2	ClH
SiO_2	P_2O_5	SO_2	Cl_2O_7

In ignorance of the number of electrons in successive rings, it is inferred that the number of mobile electrons in the outer ring cannot exceed eight, and this represents the greatest charge which has yet been observed, the minimum is zero. It is further assumed that there is a tendency for these electrons in every atom to assume either the maximum or the minimum value. Thus, if an atom has five mobile electrons, it can either lose all five and acquire a positive valency of five, or it can attract three more electrons from without, make its complement up to eight, and thus acquire a negative valency of three. Which of these two possible effects will take place, will depend upon the nature of the neighbouring atom. Thus, if a phosphorus atom be surrounded by hydrogen atoms, under the right conditions of temp., etc., its behaviour would correspond with its gaining three electrons, becoming electronegative, and forming PH_3 with a maximum valency of three ; on the other hand, if it be in contact with a strongly electronegative element like chlorine, it appears to lose five electrons, become electropositive, and to form PCl_3 or PCl_5 with a maximum valency of five. Variable valency here meets a rational interpretation, for the whole of the available electrons need not be always removed together. The work done in removing a second electron must be greater than is involved in removing the first. So with phosphorus, the force exerted by the electronegative chlorine atom may suffice to drag three electrons from the phosphorus atom, but only when the conditions are favourable is it possible to drag off another two. This does not explain the rarity of intermediate valencies between three and five.

P. P. von Weimarn assumed that all atoms have a minimum valency of six. From purely chemical considerations R. Abegg and co-workers were led to assume that every element possesses a maximum valency of 8 made up of positive and negative components according as the element is acting as an electropositive or electronegative constituent of a compound. The two valencies of opposite polarity are called **normal valencies and contra-valencies.** The normal valencies are supposed to be the stronger, and correspond with the usually accepted maximum valencies of the elements. In the case of the metals the normal valencies are positive and the contra-valencies negative ; while in the case of the non-metals, the normal valencies are negative and the contra-valencies positive. Thus :

	Na	Mg	Al	Si	P	S	Cl
Normal valencies .	+1	+2	+3	+4	−3	−2	−1
Contra-valencies .	−7	−6	−5	−4	+5	+6	+7

Thus, chlorine is univalent in HCl where it is combined with electropositive hydrogen; but it has its maximum heptavalency when united with electronegative oxygen in chlorine heptoxide. A. Werner has also shown how elements have a different valency according as they are united with electropositive or electronegative elements. The relative strengths of the two kinds of valency depend upon the nature of the associated atoms. The alkali metals are so strongly electropositive that they show little if any sign of an electronegative valency ; and fluorine appears to be too strongly electronegative to show a positive valency, for it forms no compound with oxygen. When the conditions are such that the latent contra-valencies become operative, complex compounds may be formed.

The fact that in a given family the elements with the greatest at. vol. are usually most electropositive and least electronegative, is taken to mean that when two atoms of different sizes are in contact, the attraction of the smaller atom for the electrons in the larger atom is greater than the attraction of the larger atom for the electrons in the smaller, so that the resultant force will drag electrons from the larger to the smaller atom. Again, since the at. vol. increases with the at. wt., the electropositive character of the elements in a given family increases with the at. wt.

Radioactivity.—According to J. J. Thomson's hypothesis, atoms are built of systems of rotating rings of electrons. The configuration of a system of rotating rings of electrons is dependent not only upon the number, but also upon the energy of the speed of rotation of the rings. Four electrons, for instance, may arrange

themselves at the corners of a square or a tetrahedron. If a four-square system of electrons be rotating faster than a certain critical value, they will be stable ; but if their velocity falls below the critical value, the arrangement will become unstable, and the electrons will suddenly arrange themselves in the form of a tetrahedron. Similarly, if a spinning top be rotating faster than its critical value, it will remain stable in a vertical position, but if the speed of rotation falls below this value, the top becomes unstable, and falls down ; in doing so, it gives up a considerable amount of energy. These analogies can be extended to complex groups of electrons, say an atom of uranium. Owing to the radiation of energy, the kinetic energy of the electrons is gradually reduced, and the velocity of the spinning rings of electrons can be assumed to be slowly diminishing. When the velocity approaches the critical value, the configuration of the system may be modified, and this is accompanied by an increase in the rate at which kinetic energy is lost by the radiation. When the velocity reaches the critical value, the configuration becomes unstable, an **atomic cataclysm,** or an atomic explosion occurs, and a number of electrons are detached from the original assemblage. In other words, the atom disintegrates and a part of the atom is shot off to form two or more groups of electrons. This also corresponds with the emission of α-particles and emanation from radium. As G. H. Darwin expressed it, the laws of electricity in motion prove that a community of electrons, as pictured by J. J. Thomson, must be radiating or losing energy, and therefore the time must come when it will be run down as a clock does. The aggregate will then spontaneously change into another system (or element) which needs less energy than was required in the former state. If the atoms of the emanation are built of electrons of the same type as the original atom, the process may be repeated with the sub-atoms, and so produce a series of degradation products with a long or a short life. This shows that with atoms of a special kind—*e.g.* high at. wt.—the gradual reduction of the kinetic energy of the electronic motion might produce instability within the atom. The rate of decrease of the kinetic energy may take thousands of years before it reaches its critical value, or it may take place in a very short time. The atoms of the several elements thus represent different aggregates of electrons which have proved by their stability to be successful in the struggle of the elements for a separate existence ; just as Heracleitus and Empedocles both argued that forms unsuited to their conditions must perish, while forms suited to their conditions are maintained.

A. Debierne expresses this another way. The fact that radioactive elements emit both α-particles and electrons, may be taken to show that the nucleus itself must be a complex aggregate of positively and negatively charged particles. According to the disintegration theory, an atom of uranium must emit eight α-particles before it becomes a relatively stable atom of lead. The eight positively charged particles are assumed to have come from the nucleus of uranium. The forces, which can hold eight helium atoms, or α-particles, in a volume which is small in comparison with that of the uranium atom itself, must be very different from those which are at present known. The law which determines the time at which the atomic cataclysm with the emission of α-particles shall occur is not known. A. Debierne assumed that the component parts of the complex nucleus are in a state of constant agitation like the molecules of a gas ; and, following the laws of probability, when one of the constituents of the nucleus acquires enough kinetic energy it is carried beyond the confines of the nucleus and the atom. L. Meitner has discussed the mechanism of radioactive disintegration and atomic structure.

An enthusiastic writer declares that " the corpuscular theory of J. J. Thomson has enabled chemists to explain the periodic law, valency, chemical action, etc., in terms of known facts." We are also told that more is known about the atom than about matter *en masse*. These statements are surely based on superficial views which are the result of confusing fact and fancy. The electronic model atom has but a remote analogy with the real atom. Analogy may be an invaluable aid to description, but it cannot *prove* a single fact ; *omne simile claudicat*—every

analogy limps. J. J. Thomson quite recognized the inadequacy of his model atom, for he pointed out that the number of electrons corresponding with a particular property will doubtless be different if the electrons are distributed in three-dimensional space instead of in coplanar concentric rings ; but since similar properties are associated with rings as with shells, it is probable that a system of concentric shells will present somewhat analogous properties. A more complex disposition of the electrons will obtain if the positive electrification be not uniformly distributed in the sphere. Hence, with all their imperfections, these hypotheses throw a most interesting light on Mendeléeff's series and on the possible nature of an atom ; though matter still remains an inscrutable and impenetrable mystery—and we are still puzzled, for, as W. Crookes has said : " The list of elements extends before us as stretched the wide Atlantic before the gaze of Columbus, mocking, taunting, and murmuring strange riddles which no man has yet been able to solve." Each forward step in our knowledge carries us backwards to a vaguer and remoter past.

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§ 4. Electronic Hypotheses of Chemical Combination and Valency

Truth is the daughter of time.—Francis Bacon.

In recent years there has been a constantly growing tendency to apply the electronic theory to explain chemical phenomena. It is assumed that electricity has an atomic structure, and is not continuous; and that positive and negative units of electricity are associated as constituent parts of the chemical atom. Consequently, the association of atoms to form molecules involves an investigation of the structure of fields of force exerted on the outer surface of the atom. The different hypotheses usually take one of two forms:

1. Every chemical bond between two atoms involves a *transfer* of one negative electron from one atom to the other, so that the one atom is charged positively and the other negatively.

2. If the electrons are actually displaced, J. Stark [1] considers that some phenomenon resembling the selective absorption of light takes place, and that when the electrons return to the atom, a phenomenon resembling fluorescent radiation occurs.

As previously indicated, the atom can be regarded as constituted of a positive nucleus, with n electrons rotating in orbits about a central nucleus—*dynamical hypotheses*; or, the electrons may be confined to particular parts of the structure—*statical hypotheses*. Physicists have a predilection for the former, chemists for the latter. J. Larmor, for example, compared the atom with a clock, the outer electronic shell being the pendulum, maintained in continuous vibration by the energy of the core imparted through an unknown escapement mechanism which parcels out quanta of energy. In illustration of the dynamical hypotheses, W. Kossel based a theory of chemical combination on N. Bohr's atom model, and on R. Abegg's theory of contravalencies — *vide* **1.** 5, 14. He distinguishes between outer or valency electrons, and inner electrons, and assumes that the number of electrons in the outer ring varies periodically from one to eight. He regards a ring of eight or two electrons as being exceedingly stable. His view of the structure of the argon atom, and of the molecules of hydrogen chloride and calcium oxide are represented diagrammatically in Fig. 11. The eight electrons are assumed to be constantly rotating in their orbit. In discussing the formation of complex salts like potassium chloroplatinate, K_2PtCl_6, he shows that in platinum tetrachloride, $PtCl_4$, platinum shows a normal positive valency of 4, but owing to its contravalencies, it can take up two more electrons from the potassium atom and thereby take up two more chlorine atoms. F. Kirchhoff modified W. Kossel's ideas a little, and represented, by Fig. 12, the union of an atom of oxygen—having two electrons on the inner and six in the outer ring—with two atoms of hydrogen with a single electron. M. Remy extended the theory of the formation of polar compounds to all chemical compounds.

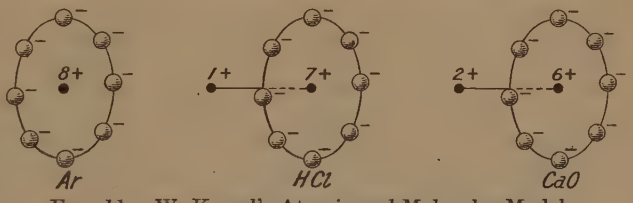

Fig. 11.—W. Kossel's Atomic and Molecular Models.

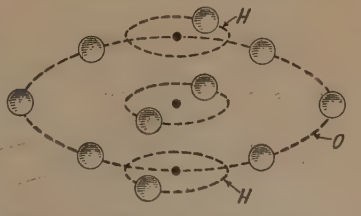

Fig. 12.—Molecule of Water, H_2O.

W. Kossel continued: When a multi-charged central atom like $Pt^{\cdots\cdot}$ is attached

to a negative charge, work is gained; the amount of this energy decreases as the number already attached increases, for the attraction of the central positively charged atom for the electronegative atoms is more and more compensated by the repulsion of those which are already attached; finally, a limit is reached when external work has to be done in order to force another negatively charged atom into the ring. By making certain assumptions as to the relative sizes of the atoms, he calculates the work, W, gained when negatively charged atoms are attached one by one from a ring round a positively charged atom. The work gained is plotted in Fig. 13, as ordinate against n, the number of negatively charged atoms, for different values of the positive charge E on the central atom. The maximum value of W shifts more and more towards larger values of n as E is increased. This means that the tendency to form complex salts increases with the increasing positive valency or charge of the central nucleus. In illustration, magnesium has two normal positive valencies, $E=2$; the curve shows that the maximum number of chlorine atoms it can attach is between three and four; and it does form the complex salt $KMgCl_3$. Similarly for antimony, $E=5$, the maximum is near six, and it forms the complex $KSbCl_6$; likewise for platinum with $Pt^{\cdots\cdot}$, $E=4$; n is between five and six; and it forms the complex K_2PtCl_6; while $Pt^{\cdot\cdot}$, $E=2$; n is between three and four; and it forms K_2PtCl_4. The agreement is not in all cases so satisfactory as this. I. Traube has discussed this subject.

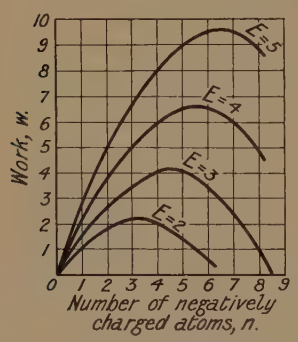

FIG. 13.—Work required to form complex Salts with an increasing Number of Negatively Charged Atoms, and an increasing Number of Nuclear Positive Charges.

N. Bohr also showed that the work required to remove an electron from the outer ring decreases with an increase in the number of electrons in the inner ring, so that the electropositive character of the elements in a given family group should increase with the at. number. This is in accord with facts. Cæsium is the most electropositive element in the alkali family. Iodine is less electronegative than any member of the halogen family; as is illustrated by the deposition of iodine on the cathode during the electrolysis of iodine monochloride. The ease with which the members of the argon family are ionized illustrates the same thing, for J. Franck and H. Hertz's ionization voltages are He, 20·5 volts; Ne, 16·0 volts; and Ar, 12·0 volts.

W. Kossel's arrangement of the electrons in the different atoms of low at. wt. is

H	He	Li	Be	B	C	N	O	F
1	2	(2)1	(2)2	(2)3	(2)4	(2)5	(2)6	(2)7
Ne		Na	Mg	Al	Si	P	S	Cl
(2)8		(2,8)1	(2,8)2	(2,8)3	(2,8)4	(2,8)5	(2,8)6	(2,8)7
Ar		K	Ca	Se	Ge	V	Cr	Mn
(2,8)8		(2,8,8)1	(2,8,8)2	(2,8,8)3	(2,8,8)4	(2,8,8)5	(2,8,8)6	(2,8,8)7

This may be compared with Table III. So long as no test is available for the stability of concentric rings of electrons, it is open to adopt any desired arrangement of electrons or rings. W. D. Harkins assumed that the relative abundance of the elements in meteorites and on the surface of the earth is dependent on the stability of the nuclei of the respective atoms, and on the stability of the aggregates of electrons. E. Rutherford believed that he has driven particles of mass 3 and charge 2 from light atoms, and inferred that these particles are of more importance than those of mass 4 in building light atoms. Against this, W. D. Harkins pointed out that at. wt. of the most abundant isotopes in F. W. Aston's list are divisible by 4, and only two are divisible by 3 as well as by 4; also the at. wt. of 87 per cent. of the elem nts in meteorites is divisible by 4; and but 0·77 are divisible by 3. F. Brösslera estimated that the mass of the hydrogen nucleus is less than the four hydrogen

atoms from which it is derived, and that during the condensation of the hydrogen nuclei, the loss of energy is $0{\cdot}029V^2$, where V denotes the velocity of light. Consequently, it is unnecessary to suppose that helium nuclei pre-exist in the nuclei of radioactive elements in order to account for the kinetic energy possessed by α-particles, for part of the energy liberated during the formation of helium nuclei within the atom from pre-existing hydrogen nuclei might be utilized in detaching the α-particles so formed and imparting to them their momentum. A. W. Hull, for example, obtains conclusions in accord with a statical theory from observations on X-ray spectra, while A. H. Compton obtains diametrically opposite conclusions

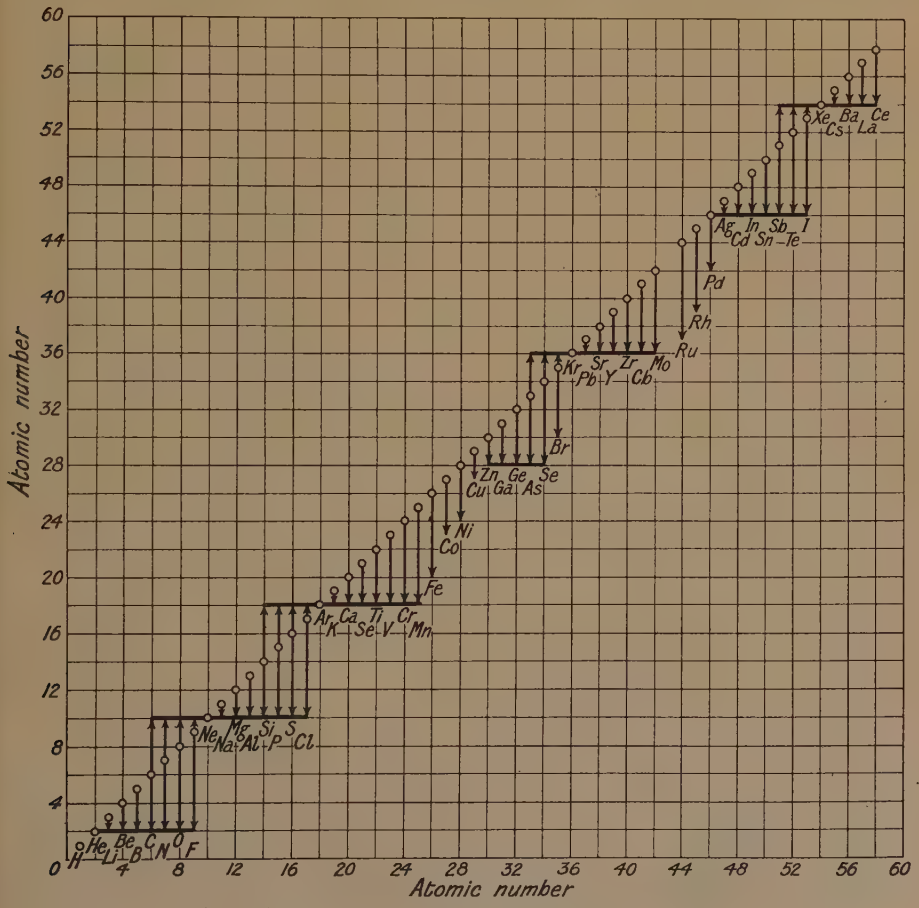

FIG. 14.—Maximum Number of Valency Electrons in the Atoms of the Elements.

in accord with a dynamical theory. J. W. Nicholson objected that coplanar concentric rings of vibrating electrons are unstable, so that if there are to be two or more rings of electrons in an atom, they cannot be in the same plane. This would make N. Bohr's theory untenable—*vide supra*. The periodic rule is taken to be represented by the periodic recurrence of rings of electrons of the same kind. The outer ring of electrons causes those electrons which take part in chemical combination. R. Abegg and G. Bodländer's normal and contra-valencies are represented by electrons which can be given up or taken on in forming compounds. W. Kossel represents this by Fig. 14. The abscissæ and ordinates represent the at. numbers of the different elements, and the arrows indicate by their length the

maximum number of electrons which each atom can give or receive in forming compounds. F. Urbach has discussed an analogous hypothesis.

The hypotheses of W. Ramsay, J. Stark, J. J. Thomson, G. N. Lewis, I. Langmuir, etc., favour the statical view of the structure of the atom. In **W. Ramsay's theory of rotating electrons,** the fixed electrons were assumed to rotate in circular orbits; and the valency electrons to rotate in small circles at definite places on the surface of the atom. The orbits of the latter were thus parallel to some equatorial plane fixed in the atom, the orbits of the different valency electrons need not necessarily have the same diameters; and while some electrons may revolve clockwise, others might revolve anti-clockwise relative to the nearest poles of the sphere. Electropositive elements differ from electronegative elements in the direction of rotation of the electrons. The formation of molecules was explained by the magnetic attraction due to the rotating electrons, which arranged themselves in the molecules so as to permit the maximum magnetic flux through the planes of the electronic orbits. W. E. Garner discusses a modification of this hypothesis. A. L. Parson also assumed that the electron itself is a rotating ring of negative electricity, and is therefore a minute permanent magnet, and he called such an electron a *magneton*. The magnetons at the surface of different atoms exert magnetic and electrostatic forces on each other which result in chemical combination. A. E. Oxley also suggested that the electrons revolve in small circles about stable positions in the atoms. A. H. Compton, A. D. Fokker, D. L. Webster, A. H. Crehore, K. Herrmann, H. S. Allen, W. Lenz, W. Pauli, etc., have discussed the magnetic polarity of atoms. T. R. Merton inquired if the orientation of the atoms in crystals is regular or at random, on the assumption that the atom has an axis perpendicular to the plane in which the electrons are rotating. If the α-particles are related to the orientation of the axis, the α-ray activity from the different faces of a radioactive substance might differ per unit area exposed. No difference was detected within the limits of the method of measurement available.

W. Ramsay in imagination materialized the electrons by stating that "electrons are atoms of the chemical element electricity; they possess mass; they form compounds with other elements; they are known in the free state, *i.e.* as molecules; and they serve as bonds of union between atom and atom." He symbolized it by E; and the valency of an element is determined by the number of electrons which an element gains or loses under a given set of conditions. R. C. Tolman, M. von Laue, and H. A. Wilson have discussed the thermodynamics of what they call *electron gas*.

(*a*) In one form of **J. Stark's hypothesis** the units of positive electricity are supposed to be situated on the surface of the atoms, not as uniformly charged zones, but rather conc. at certain points, and the neutralizing negative electrons are assigned definite positions on or near the surfaces of the atoms. When two atoms are united together, the negative electrons hold the positive atoms each to each, as illustrated diagrammatically in Fig. 15, where the dotted lines represent tubes or lines of force. Otherwise expressed, **when two atoms are united chemically, they are held together by electrons common to both atoms,** each pair of electrons linking the atoms together are eq. to one univalent bond of the ordinary valency doctrine. In J. Stark's theory, compounds are formed when the lines of force from one of the valency electrons stretches to the positive area on the other atoms. With strongly polar bodies, an electron is drawn almost wholly to the atom which holds it in combination. A primary valency is an effect of a pair of negative electrons whose field binds the atoms together. The stray electric field in the space about the molecule produces the so-called residual affinity.

FIG. 15.—Saturated Valency.

(*b*) In J. J. Thomson's hypothesis of **directed valencies,** the electric forces which keep the atoms together originate in a *displacement* of the positive and negative electricity in each atom; and, as a result, each atom acts like an electric doublet and attracts another atom, much in the same way that two magnets attract one another.

J. J. Thomson's theory starts from the assumption that an atom is an aggregate of negative electrons with a sphere of positive electrification. The charges (i) may or (ii) may not counterbalance one another, leaving the atom either electrically neutral or polarized. that is, charged with a surplus of positive or negative electricity. A pair of balanced charges is called an **electric doublet,** and W. Sutherland suggested the hypothesis that the peculiar force exerted by an atom is the same as if each atom carried an electric doublet whose moment is characteristic of the atom. W. Sutherland's atoms therefore characterize compounds of the first class, but not the second. K. Kallmann and F. Reiche studied the passage of molecules with electric dipoles through unhomogeneous electric fields.

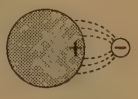

FIG. 16.—Unsaturated Valency.

The field of electric force about the molecules of a compound.—From the known properties of electrified bodies, it is inferred that a field of electric force must envelop each atom no matter whether the opposite charges wholly or partially counterbalance one another, because the positive and negative electrons are *ex hypothesi* unable to destroy one another. The neutralization of two opposite charges annuls the electric field at a comparatively large distance from the atoms. Coulomb's law applies only to comparatively large distances, and not at distances comparable with the dimensions of the atoms. Some unrecognized cause seems to prevent positive and negative electrons approaching within less than a certain distance. Consequently, even an electrically neutral atom will have a field of force which (i) will not be uniformly distributed about the atom ; and which (ii) will probably diminish in intensity more rapidly than the inverse square of the distance. The field of force emanating from the charges in the atom will give rise to (*a*) *intramolecular attractions* whereby the charged atom affects the other atoms associated with it in the molecule ; but it will also give rise to (*b*) *intermolecular attractions* because the field of force of an atom will also attract the atoms in other molecules, and so produce phenomena like the surface tension of liquids, latent heat of evaporation, cohesion of liquids and solids, etc. Accordingly, chemical compounds can be divided into two classes.

I. Non-polarized molecules with uncharged or neutral atoms.—The individual atoms of the molecule are neutral, for the constituent atoms are charged with equal amounts of positive and negative electricity, and there is no surplus or excess of the one kind over the other. The atoms are held together by one or more doublets on each atom. Among the **non-polar molecules** are H_2, O_2, He, N_2, Cl_2, CO, CO_2, CS_2, CCl_4, C_6H_6, N_2O, etc.

II. Polarized molecules, or molecules with charged atoms.—The individual atoms within the molecules carry an excess of positive or negative electricity so that the whole molecule is charged, and, accordingly, exerts larger forces upon the atoms of neighbouring molecules than would be the case if the atoms were neutral. There is supposed to be an actual transfer of an electron from one atom to another in those molecules. The chemical reactivity, specific inductive capacity, surface tension, cohesion, tendency to form molecular complexes, and other qualities of such compounds are found to be highly developed. Among the **polar molecules** are grouped H_2O, NH_3, HCy, SO_2, HCl, CH_3OH, C_2H_5OH, CH_3Cl, etc.

G. N. Lewis, R. W. G. Wyckoff, S. H. C. Briggs, and W. C. Bray and G. E. K. Branch also have emphasized the fact that there are two types of chemical compounds which can be designated polar and non-polar, and which they regarded as coinciding approximately with what are usually known as inorganic and organic compounds. These compounds are typified respectively by potassium chloride and methane. Nevertheless, some inorganic compounds are predominantly non-polar, and some organic compounds, at least in certain parts of their molecule, are strongly polar. G. N. Lewis contrasts the properties of the extreme members of these two types by means of Table IV. He continues : " All of these properties with respect to which fundamental distinctions have been made between the two types, and which seem so unconnected, are in fact closely related, and the differences

are all due to a single cause. Even before making any more special hypothesis we may very safely assume that the essential difference between the polar and the non-polar molecule is that, in the former, one or more electrons are held by sufficiently weak constraints so that they may become separated from their former positions in the atom, and in the extreme case pass altogether to another atom, thus producing in the molecule a bipole or multipole of high electrical moment. Thus in an extremely polar molecule, such as that of sodium chloride, it is probable that at least in the great majority of molecules the chlorine atom has acquired a unit negative charge and therefore the sodium atom a unit positive charge, and that the process of ionization consists only in a further separation of these charged parts.

If then we consider the non-polar molecule as one in which the electrons belonging to the individual atom are held by such constraints that they do not move far from their normal positions, while on the polar molecule the electrons, being more mobile, so move as to separate the molecule into positive and negative parts, then all the distinguishing properties of the two types of compounds become necessary consequences of this assumption, as we may readily show. From the fact that in the polar molecule "the constraints which operate against a separation of the charges are already weak, it follows that these charges may be further stretched in the electric field, and that bipoles or multipoles which already exist in the substance may, by rotation, orient themselves in the electric field, thus producing a large displacement current and therefore a high dielectric constant. Now as the difference between the dielectric constant of a substance and that of free space measures directly the number of free charges in the substance multiplied by the average distance through which these charges move under the influence of a definite electric field," it follows that the dielectric constants of polar substances must be relatively greater than those of non-polar type. Also it follows that polar substances may be readily ionized and will form ionizing solvents. That is, such substances are good conductors of electricity (electrophiles).

TABLE IV.—THE PROPERTIES OF POLAR AND NON-POLAR COMPOUNDS.

Polar.	Non-polar.
Mobile	Immobile
Reactive	Inert
Condensed structure	Frame structure
Tautomerism	Isomerism
Electrophiles	Non-electrophiles
Ionized	Not ionized
Ionizing solvents	Non-ionizing solvents
High dielectric constant	Low dielectric constants
Molecular complexes	No molecular complexes
Association	No association
Abnormal liquids	Normal liquids

The distribution of the electric charges within the molecule.—Each element has its own specific attraction for negative charges, thus, sodium exerts a less attraction for negative charges than chlorine; otherwise expressed, sodium is more electropositive than chlorine. With carbon monoxide, although the opposite charges on the two atoms neutralize one another, yet the oxygen has a greater attraction than carbon for a negative charge. Hence, a certain amount of work is available in the transfer of a negative charge from the atom in which the attraction is weak to an atom in which the attraction for the negative charge is strong. Accordingly, when a neutral electropositive atom is united with an electronegative atom, the negative charge tries to pass from the former to the latter and electrify it negatively. Why does not the transfer always take place? J. J. Thomson assumes that electricity

has an atomic structure, and must pass in definite units from one point to another, and therefore a whole charge must be transferred or none at all. He illustrates the action by diagram, Fig. 17. Each atom C and O carries a balanced positive and negative charge. The O is more electropositive than the C, and there is therefore a tendency for a negative charge to pass from the C to the O atom; but this tendency does not suffice to overcome the attraction of the positive charge carried by the C atom. This latter is diminished by bringing up another atom represented by the dotted line, Fig. 18. This helps the passage of the negative charge across to the O atom. Thus, the atoms of a compound may be uncharged when isolated, and yet become charged when the compound is in a liquid state, or when the atoms are combined to form more complex molecules. The term **intramolecular ionization,** by the way, is applied by J. J. Thomson to the process by which the atoms of a molecule get charged electrically.

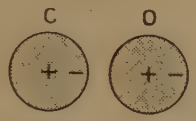

FIG. 17.—Carbon monoxide, CO, with neutral atoms.

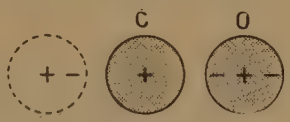

FIG. 18.—The charging of a carbonyl, CO, radicle.

J. J. Thomson compares the two atoms of, say, carbon monoxide with the two coatings of a Leyden jar; so that the whole molecule behaves as if it were a Leyden jar of small capacity. It is known that the smaller the capacity of a jar, the greater the amount of energy required to transfer, say, q units of electricity into the jar. If the available energy be less than this, the transfer of, say, a single negative charge from a carbon to an oxygen atom will not occur, and *vice versâ*. By increasing the capacity of the "jar" a transfer might occur which would otherwise be impossible. Hence, if another molecule be added to a certain atomic system, its capacity might be increased and accordingly less work might be required to transfer a charge from an electropositive to an electronegative atom.

Platinum tetrachlorodiammine, $PtCl_4(NH_3)_2$, is not an electrolyte, because its atoms are electrically neutral. Add another molecule of ammonia to get $PtCl_4(NH_3)_3$, and the resulting compound is an electrolyte with a mol. conductivity of 97; this number rises to 228 with the addition of another molecule of ammonia to form $PtCl_4(NH_3)_4$; and up to 553 when two more molecules of ammonia are added to form $PtCl_4(NH_3)_6$. Thus, as the molecules of ammonia are increased, the charges carried by the atoms increase rapidly. Carbon monoxide is neutral, but when it enters as a carbonyl radicle into organic compounds—like acetone, $(CH_3)_2CO$; aldehyde, CH_3COH; etc.—it raises their specific inductive capacity because the CO radicle becomes charged on entering the compound. The proximity of other atoms increases the capacity of the system sufficient to allow the transfer in question. Mere contact with the other atoms promotes intramolecular ionization. In some cases, some of the radicles or atoms may carry one or more charges, and other atoms may be electrically neutral. The hydroxyl radicle, OH, may exist in a molecule in two states according as the oxygen atom carries one or two negative charges. If the oxygen atom carries one charge, the radicle $O^-—H^+$ will form an electric doublet; and if two charges—as is probably the case with water—there must be a positive charge on some other radicle not the hydroxyl group, and there will be two doublets in the molecule. J. J. Thomson suggests that the difference in these two states determines whether the OH radicle acts as an acid or as a base. Acidic hydroxyl is represented by $O^-—H^+$, and basic hydroxyl (of water) $O^=—H^+$, for if the molecule $RO^-—H^+$ be in soln. and surrounded by H^+ and $O^=—H^+$ ions, arising from the dissociation of water, the H^+ ion of the given molecule would unite with the $O^-—H^+$ of the water, and leave an excess of H^+ ions in soln. so that the molecule $RO^-—H^+$ would have acidic properties; on the other hand, in the molecule $R^+—O^-—H^+$, the $O^=—H^+$ of the molecule would unite with the H^+ from the dissociation of the water and leave an excess of $O^=—H^+$ ions in the water, and the molecule would have basic properties. The more electropositive the element R in

the ROH molecule, the more likely is an electron to be transferred from the R to the O atom, and accordingly the more likely is the oxygen to acquire a second charge and show basic properties.

Valency electrons or corpuscles.—J. J. Thomson further suggests that each atom may contain negative electrons related to the atom in two ways: (i) *Immobile constitutional or fixed electrons.* Some of the electrons are firmly fixed at or near the core of the atom; they are not free to adjust themselves so as to cause the atom to attract other atoms into its neighbourhood; and they take no part in chemical reactions. (ii) *Mobile or valency electrons.* Some of the negative electrons are supposed to be located near the surface of the atom, and they are free to move about and set themselves into position under the influence of external electrical fields. They are linked with the central positive charge of the atom by lines of force. The mobile electrons, which J. Stark called *Valenzelektronen*, enable the atoms to hold on to one another and form a bond between joined atoms. The number of mobile corpuscles determines the valency of the atom so that a univalent atom has one, a bivalent atom, two, and a septivalent atom has seven mobile electrons. The mobility of the electrons is an essential condition necessary for one atom to exert any considerable attraction on another. For example, if an atom with one mobile negative electron—Fig. 19—and another atom with its negative electron—Fig. 20—were in contact, the two atoms would attract or repel one another as illustrated in the diagrams. If, however, the electrons are free to move, they will be driven apart until the positive charge of the one atom is nearer to the negative charge of the other, and the atoms would then attract one another. The negative electron has very little inertia and, if free, can be driven round at once. The initial repulsion would therefore be momentary and attraction would be the final result. If the electron was fixed, it could not swing round without carrying the whole atom, which is a comparatively heavy body difficult to move. As a result, when the electrons are mobile, the atoms are kept together, but when the electrons are fixed, the atoms will have comparatively little attraction for one another. When the negative corpuscles of the atom are so firmly fixed as to be incapable of exerting any great attraction on other atoms surrounding it unless they are in particular positions, the valency of the atom is said to be sat., for the satisfaction of a valency is essentially the fixing of one of the mobile negative electrons.

FIG. 19.—Repulsion.

FIG. 20.—Attraction.

Fixing the valency electrons.—Assume that each negative electron in an atom is the origin of a line or tube of force. If the atom is alone, the line of force will return to the same atom and end on its own positive charge as illustrated diagrammatically (Fig. 21). The negative electron is still free to move. Consequently, an electron will not be fixed when the atom is by itself, but only when the line of force from the electron is anchored to an opposite charge on another atom *B*, Fig. 23. The electron is then deprived of its mobility, and is unable to attract another atom.

FIG. 21.—Tube of Force of a Mobile Corpuscle.

Case I. If the two atoms be electrically neutral, a similar tube of force will pass from each negative electron on each atom to the positive charge on the other atom, as illustrated diagrammatically (Fig. 23). Hence, with neutral atoms, for each tube of force which leaves an atom there will be a return tube—as many will go out as come in. Two electrons are involved in holding together two univalent neutral atoms. If the atoms are each bivalent, two tubes of force will leave each atom and two return; in general, **in compounds with neutral atoms the total number of lines of force between the constituent atoms is double the chemical valency.** This means that J. J. Thomson would represent each chemical valency by *two* bonds between the atoms of a molecule when the con-

stituent atoms are electrically neutral. It does not follow that if the atom A sends a tube of force to another atom B, it must receive one from the *same* atom B, for the return tube may come from *another* atom. The necessary condition is that **the number of tubes of force which leave an atom must be equal to the number which return.** With this understanding, certain combinations can be explained which appear to be anomalous in the light of the old valency hypothesis. If hydrogen be univalent, a combination like H_3 was considered impossible on the other hypothesis; but the hydrogen molecule has neutral atoms, with two tubes of force issuing from each. Consequently, the molecule H_3, that is—

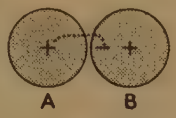

FIG. 22.—Union of Charged Atoms.

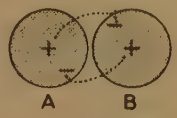

FIG. 23.—Union of Neutral Atoms.

$$\begin{matrix} & & H \\ H & \triangle & H \end{matrix}$$

is thus quite compatible with the hypothesis, so also is a molecule H_n. Again, with monatomic silver, AgCl, $AgCl_2$, $AgCl_3$, and $AgCl_n$ are all possible valency compounds in this extension of the older valency hypothesis. The trouble with the hypothesis is that it apparently explains too much. There is no known evidence of the phenomenon—bi- or octo-valent carbon—with organic compounds, although a divided valency is sometimes observed in the arrangement of the atoms in crystals —*e.g.* the X-radiograms of magnetite.

Case II. If the two atoms be charged electrically.—We have seen that an electron will be fixed when its tube of force passes out of its atom and ends upon some other atom (Fig. 23). If one of the negative electrons (Fig. 22) be dragged from one atom, A, to the atom B, the electron would follow its tube of force which left the atom A, and the tube of force would shrink up in the atom B, and only one tube of force would connect the two atoms. When a number of electrons are transferred from one atom to another, the number of tubes of force between the two atoms will be halved, because after the transfer no tube of force will leave the electropositive atom, and none will enter the electronegative atom. The one atom, B, would thus be positively charged and the other, A, negatively charged. Hence, **in compounds with charged atoms, the number of tubes of force between the constituent atoms will be equal to the chemical valency.** The tube of force is then eq. to the bond or bar of the regular structural formulæ employed by chemists, and the valency bond is only applicable when the constituent atoms are charged electrically. If the constituent atoms are electrically neutral each valency bond must be doubled if it is to represent a tube of force. The chemist's hyphen or bond is thus related with the physicist's tube of force.

I. Langmuir has pointed out that valency may be exhibited in three different ways: (i) *Positive valence*, represented by the number of electrons an atom can relinquish; (ii) *Negative valence*, represented by the number of electrons an atom can receive; and (iii) *Co-valence*, represented by the number of pairs of electrons an atom can share with its neighbour.

Saturated and unsaturated compounds.—It follows from the preceding discussion that **when each of the mobile electrons in an atom is anchored by a tube of force to a neighbouring atom, the average attraction of that atom for other atoms is reduced to a minimum.** J. J. Thomson further shows that if the molecule of a compound is to exist in a stable form, (i) The molecules must not exert a sufficiently large attraction on the neighbouring atoms to cause them to unite and form other molecular systems. This will be the case when the work required to separate the two molecules under consideration is small compared with the average kinetic energy of the molecule at the temp. *T*. (ii) The attractions between the atoms of the molecules must be great enough to prevent a separation

when the molecule collides with other molecules. This will obtain if the work required to separate the atoms is large compared with the average kinetic energy of the molecule at the temp. T. These conditions are greatly influenced by temp. Thus, with iodine vapour, the monatomic molecule may exist in a stable form at a high temp., and pass into more complex diatomic molecules at lower temp.

If carbon monoxide is a stable compound when electronegative carbon is united with the more electronegative element oxygen, why does not CCl_2 also form a stable compound ? J. J. Thomson answers this question as follows : As already indicated, an atom, even when sat., must produce an electric field in its neighbourhood. This field must restrict the freedom of motion of molecules of the corpuscles in neighbouring atoms. If the electric field due to the oxygen atom in carbon monoxide be very strong, then, even though but two of the four mobile corpuscles of the carbon atom are bound to the oxygen by tubes of force, the other two will be exposed to so strong an electric field that their mobility is reduced. As a result, the attraction of the carbon atom on other atoms is reduced. The amount of residual attraction, so to speak, depends upon the strength of the electric field in the carbon atom produced by the oxygen atom. If the electric field with the CCl_2-system be smaller than that produced in the CO-system, it follows that the latter will behave more like a sat. molecule than the former, and the carbon monoxide molecule, in consequence, might exist in a free state when the CCl_2 could not.

It might be argued that in a compound like ethane, C_2H_6, with electropositive hydrogen atoms, and electronegative carbon atoms, the two carbon atoms are in a different electrical state, because the tubes of force from three hydrogen atoms end on each carbon atom, and a tube of force from one carbon atom must end on the other ; accordingly, the potentials of the charges on the two carbon atoms must be different. This is illustrated diagrammatically in Fig. 24. Similar remarks apply to acetylene and probably also to ethylene linkages. No phenomenon has yet been noticed which would justify this conclusion in the case of ethane, but in the case of doubly and triply linked combinations, several properties—mol. vol., index of refraction, etc.—are markedly different from what they are with the carbon atoms all singly linked together.

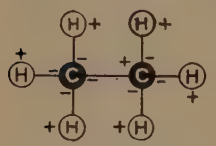

Fig. 24.—Ethane, C_2H_6.

It is doubtful if every chemical bond involves the transfer of an electron from one atom to another ; but, according to J. J. Thomson, it is more probable that the electric force which keeps the atoms of a molecule together, is not due to one atom being charged positively and another negatively, but to the displacement of the positive and negative electricity in each atom. Thus, each atom acts like an electric doublet and attracts another atom much in the same way that two magnets attract one another. According to S. J. Bates, it is not necessary to assume that an electron moves from one atom to another for the atoms to be held together by electric forces, because (i) there is no evidence to justify the assumption that two atoms of an elementary gas like hydrogen, or two methyl radicles in ethane, are so different that one would be positively and the other negatively electrified. The two halves of each molecule react in an identical way ; if they reacted differently, there should be more cases of isomerism than have been observed. (ii) Positive ray analysis shows that there is no relation between the greatest number of electrons an atom can lose and any chemical property such as the valency of an element ; but it rather depends on its at. wt. Thus, the inert gas helium readily loses two electrons, and argon may carry one, two, or three positive charges, and krypton four. The carbon atom can carry no more than two charges, whereas it would be expected to carry four. (iii) In a dissociating gas, new molecules are being continuously decomposed while others are being formed ; conductivity measurements, by J. J. Thomson, show no sign of any difference in the number of charged atoms or molecules than is present in a gas stable under the given conditions ; P. J. Kirkby also concluded that the atoms of oxygen in water are not bound by electrostatic forces because the atoms of oxygen

when separated are not charged electrically ; nor did P. J. Kirkby and J. E. Marsh find any signs of the separation of charged atoms during the explosion of azoimide.

The effect of chemical combination on the structure of the atom.—A change in the internal structure of atoms in combination would explain why the properties of a compound may differ markedly from those of the contained elements ; but the numerous atomic or additive properties show that the contained atoms of a compound may retain their individuality in combination ; and the X-radiograms of crystals show that the contained atoms are juxtaposed and do not interpenetrate one another. Radioactivity also is not affected by chemical combination. The changes of energy involved in ordinary chemical actions are puny in comparison with those inherent in the atom as revealed by radioactivity. The free interatomic energy of the atoms in a molecule is but a small fraction of their intra-atomic energy. The loss or gain of electrons which occurs in chemical combinations must be accompanied by a more or less profound internal transformation of the atom ; this is evidenced on the ionic hypothesis in the difference which occurs between the activity of atoms and their ions ; a difference, say G. Ciamician and M. Padoa, *que la seule présence d'une charge électrique ne suffit pas á expliquer, quoi qu'on ait dit ou écrit á ce sujet.* An atom or molecule can acquire an electric charge without differing greatly from the neutral atom or molecule—*e.g.* ionized and non-conducting air. They add therefore that *the essence of chemical phenomena is a modification of the internal structure of the atom ;* and inquire : Does the form of the atom vary in different types of chemical combination or does it remain constant ? Certain elements retain the same chemical habit throughout the different types of combination. For example, carbon monoxide, hydrocyanic acid and the carbylamines, triphenyl-methane and the more complex analogous compounds do not differ essentially from the corresponding compounds of carbon in which the atom acts as tetravalent. By analogy we may say that the oxygenated compounds of chlorine possess common chemical characteristics in spite of the different amounts of oxygen contained, and the same thing is true of the compounds of nitrogen. On the other hand, certain other elements undergo so great a change of character in passing from one type of combination to another that one might think that the same atom consists of two or more different elements. Thus the knowledge of cupric salts could not enable us to predict the existence of the cuprous salts ; and how remarkable does thallium appear because of the great difference which exists between the thallous and the thallic compounds ! The same thing is true of the compounds of manganese, if we compare the manganic and the permanganic acids with the manganous salts ; or in the compounds of chromium, the derivatives of chromic acid with the salts of the sesquioxide. When we take into account such facts as these, it seems necessary to believe that in the case of some elements the form of the atom may vary according to the type of the combination, and consequently that there are elements whose atoms are polymorphous. In the case of some of them, such as carbon, for example, the variation of the valence does not imply the modification of the form of the atom, for the valencies remain free ; in the case of others, different forms of the atom correspond to different types of combinations ; for example, the atom of copper is dimorphous.

E. Kohlweiler argues that chemical processes have their origin in the nucleus of the atom, although the outer electrons may play a secondary part. If electrons were the only factors involved, the α-particle ought to be bivalent, whereas it has an affinity only for electrons. Ions occur in canal rays with positive charges which do not correspond with their chemical valencies. Nuclear structure and charge are the fundamental data of the chemical elements.

The constituent atoms of many compounds carry electric charges. The following indicates the chief evidence which has been adduced to support the view that the atoms in the molecules in some compounds are charged, and in other compounds uncharged. One of the most direct proofs of the existence of bodies in which the constituent atoms are electrically neutral is the absence of any signs

of electrical conductivity during the dissociation of, say, nickel carbonyl, carbon monoxide, oxygen molecules, etc. This result is confirmed by the positive ray analysis. On the other hand, with gases like hydrogen chloride, hydrogen cyanide, ammonia, etc., the opposite conclusion is drawn respecting the constituent atoms of the dissociating gas.

The specific inductive capacities, k, of compounds with presumably charged atoms, are markedly different from those with neutral atoms. Thus, the numerical value of $k-1$ is

Constituent atoms neutral.				Constituent atoms charged.			
Air	H_2	CO_2	CO	H_2O	NH_3	HCl	CH_3OH
0·00059	0·00026	0·00094	0·00069	0·0070	0·0071	0·0025	0·0060

The specific inductive capacity of compounds whose molecules have charged atoms diminishes rapidly with a rising temp. For instance, with methyl alcohol, as the temp. rises from 93·2° to 148·6°, the value of $k-1$ diminishes more than 25 per cent. On the other hand, this constant is virtually independent of temp. with compounds whose constituent atoms are electrically neutral. The explanation turns on the fact that a molecule with charged atoms would try to set itself in a definite direction when placed in an electric field. The greater the proportion of the molecules of the compound which succeed in maintaining themselves in this position, the greater the specific inductive capacity. The mutual collisions of the molecules of a gas knock their axes out of line and prevent the axes of a certain proportion of the molecules from pointing in the right direction. The more violent the collisions the more the axes will be disturbed, and the less the relative number of molecules which contribute to the specific inductive capacity. Certainly, the molecules of a compound with uncharged atoms will have positive and negative charges induced at opposite poles when in an electric field, but the movements of the molecules will not disturb the relative position of these induced charges. The sphere might be knocked about by collisions, but that need not interfere with the electrification. Hence, the specific inductive capacity of compounds with uncharged atoms is not much affected by changes of temp.

As previously indicated, L. Bloch has shown that when a gas bubbles through a liquid such as water, alcohol, or acetone—in which the atoms of the molecules presumably carry electrical charges—the gas, as it emerges from the liquid, is mixed with positive and negative ions; whereas with liquids like paraffin oil or benzene, the emerging gas is not much affected. This is explained by assuming that fresh surfaces are continually produced as the gas bubbles through the liquid, and these surfaces have an amount of energy, per unit area, equal to the surface tension. Since this energy tends to a minimum, the effect of the action between the molecules which produce surface tension will be to promote any change which diminishes the surface tension at a fresh surface. Hence, the dissociation of a molecule of a compound will be favoured if a layer of dissociated atoms would give a smaller surface tension than the undissociated liquid; if the atoms of the molecules be charged the products of the dissociation will produce ions which are carried along and charge the gas electrically.

J. J. Berzelius considered that "the regular form of crystalline solids demonstrates an effort on the part of their atoms to touch one another by preference in certain points," and that this "can be no other than an electric or magnetic polarity." If one end of a crystal of tourmaline be dipped in liquid air, the cooled end contracts and sets up internal strains which must involve a rearrangement of the molecules inside the crystal. J. J. Thomson explains this by assuming that the molecules of tourmaline are electrified even at ordinary temperatures, and that the effect is masked by a conducting film which covers the crystal and acts as a shield. As soon as the internal arrangement of the crystal is disturbed, the skin can no longer counterbalance the internal electrification and a temporary electrification appears. Crystals of boracite, topaz, smithsonite, prehnite, scolezite,

aximite, etc., also exhibit pyroelectrification. The phenomenon may not prove Berzelius' hypothesis, but it certainly shows that a class of bodies may exist in which the atoms of the molecules are charged electrically.

Modifications of the theory have been proposed by K. G. Falk, R. F. Brunel, J. M. Nelson, H. T. Beans, H. S. Fry, W. C. Arsem, W. A. Noyes, C. R. Bury, E. J. Cuy, W. C. Bray and G. E. K. Branch, W. M. Latimer and W. H. Rodebush, G. N. Lewis, I. Langmuir, G. A. Perkins, H. I. Cole, H. Geiger, M. C. Neuburger, A. Sommerfeld, L. Zehnder, A. Lapworth, M. L. Huggins, J. Steiglitz, A. Duvallier, A. Magnus, W. Hughes, H. G. Grimm, G. L. Clark, A. D. Fokker, E. Yamazaki, R. A. Millikan, L. Meitner, J. K. Marsh and A. W. Stewart, R. M. Caven, J. D. M. Smith, W. O. Kermack and R. Robinson, J. N. Friend, etc.

Accepting the hypothesis that an atom of a univalent element has one disposable electron, that of a bivalent two, etc., J. J. Thomson (1922) argued that there must be in the crystal of a univalent element such an arrangement of atoms and electrons, that, for each atom, there is one electron; two electrons for each atom in a crystal of a bivalent atom; etc. He further assumed that this condition determines the forms in which the various elements can crystallize, and showed that, without further assumptions of physical constants such as dielectric constant, bulk modulus, frequency, etc., it is possible to calculate values for the crystal structure of the different elements which agree closely with observations.

Molecular compounds, or complex compounds.—In the so-called molecular compounds the simpler molecules are supposed to be held together by residual affinity (or secondary valencies) represented by stray electric fields around the molecules, and "these forces," says J. J. Thomson, will be exerted by the atom, not merely on the atoms which are associated with it in the molecule of a chemical compound, but also on the atoms in other molecules, giving rise to forces between the molecules, and thereby producing the intrinsic press. and surface tension of liquids, latent heat of evaporation, cohesion of solids and liquids, the rigidity of solids, and so on. These physical phenomena are the effects of forces between different molecules, whereas chemical affinity and chemical phenomena in general are the effects of forces having the same origin, but acting between the atoms of the same molecule. W. Jacobs, and R. D. Kleeman discussed the electric doublet theory in chemical reactions. H. W. Smith regarded secondary valency as the force binding molecules together, and not due to stray fields of force or to the operation of attractions acting according to some power of the distance. He asserts that the forces binding molecules are rhythmic in nature and not subject to ordinary electromagnetic laws. Secondary valency bonds have been discussed by D. Strömholm, F. Hocheder, J. A. N. Friend, G. F. Hüttig, S. H. C. Briggs, A. E. Lacomblé, etc.

In **G. N. Lewis' theory of the cubical atom,** it is postulated: (i) In every atom is an essential kernel which remains unaltered in all ordinary chemical changes and which possesses an excess of positive charges corresponding in number to the ordinal number of the group in the periodic table to which the element belongs. (ii) The atom is composed of the kernel and an outer shell, which, in the case of the neutral atom, contains negative electrons equal in number to the excess of positive charges of the kernel, but the number of electrons in the shell may vary during chemical change between zero and eight. (iii) The atom tends to hold an even number of electrons in the shell, and especially to hold eight electrons which are normally arranged symmetrically at the eight corners of a cube. A diagrammatic representation of the atoms ranging from lithium to fluorine is shown in Fig. 25. Lithium has one normal positive valence represented by one electron which can be readily detached; fluorine has one normal negative valence and seven contravalencies; it can therefore readily take up another electron, completing a group of eight; it then resembles an atom of neon with the difference that (i) the fluorine has then one negative charge whereas neon is neutral; and (ii) the nuclear charge is not so great. If the seven electrons be removed from fluorine, it resembles an

atom of helium except for the nuclear charge. It is further assumed that two or eight electrons are very stable; and hence the inertness of the helium family. Every other type of atom can readily receive or relinquish electrons formally to resemble the members of the helium family. Thus, an atom of sodium by relinquishing one electron formally resembles neon, while an atom of sulphur by receiving two electrons formally resembles argon. When a lithium atom has given up one electron, the residue $Li^{\cdot}$ is regarded as the kernel of the atom which is supposed to contain three positive charges and two electrons. Similarly with the atoms of the

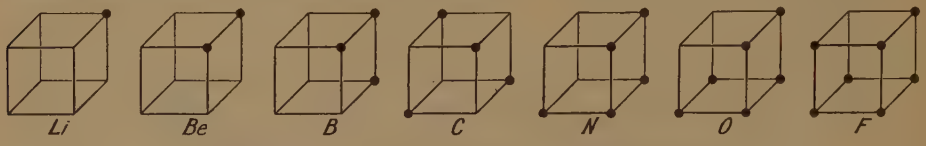

FIG. 25.—G. N. Lewis' Theory of Cubical Atoms.

other elements. In chemical combination, say HCl, or LiCl, the more electropositive element gives one electron to the electronegative element so as to make a group of eight. Similarly, an atom of calcium, with its two detachable electrons, gives up two electrons to an atom of oxygen to form a group of eight, forming a molecule of calcium oxide. In forming ammonia, three hydrogen nuclei are attached by means of electrons to the unoccupied places on the nitrogen atom; at the same time, the nitrogen atom is able to give an electron to another hydrogen nucleus. The result is an NH_4-group with one readily detachable electron. The NH_4-group thus resembles the atom lithium, sodium, etc. From observations on the compressibility of salts of the alkali metals, A. Landé and co-workers also assumed that the atom has a cubic symmetry; and it is suggested that the electrons are arranged at the corners of a cube where they can rotate in orbits while preserving the cubic symmetry of the atom. These tridimensional models were criticized by A. Smekal, and A. Sommerfeld discussed the equilibrium of systems of cubic atoms. J. J. Thomson showed that when the electrons are arranged symmetrically in an atom, the displacement of an electron by an external force will always be in the direction of the force, and the ratio of the displacement to the force will be independent of the direction of the force. The same condition does not hold when the atom is unsymmetrical, for the displacement of the electron is not in the direction of the force.

I. Langmuir has remodelled the preceding hypotheses, and produced a statical hypothesis which is known as **I. Langmuir's octet theory of atoms.** It is closely related to G. N. Lewis' cubical theory, and includes many of the suggestions from W. Kossel's dynamical theory. It is assumed that the chemical inertness, the high ionizing potential, the low b.p., etc., of helium show that the arrangement of the electrons in helium is more stable than that of any other element. A pair of electrons thus represents a very stable group, and the evidence indicates that a similar pair of electrons is contained in the atoms of lithium, beryllium, etc. These two electrons are supposed to be symmetrical with respect to an equatorial plane, but not in the plane, Fig. 26. The symmetry is thus that of the tetragonal system like the earth with a polar axis *cd*, and an equatorial plane *ab*. The continuity in the *K*- and *L*-radiations show that there is no abrupt change in the internal layers of electrons about the nuclei of the atoms of elements of low and high at. number. The properties of neon likewise show that its electronic system is more stable than that of any element other than helium, and its ten electrons are presumably arranged as a set of two and a set of eight. It is assumed that the great stability of the octet is a result of the geometrical symmetry of the arrangement of eight electrons at the corners of a cube. This explains why an arrangement of seven or nine electrons is not so stable.

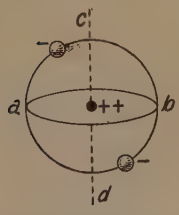

FIG. 26.—Helium Atom.

The eight electrons arrange themselves in a second shell concentric with the other; four electrons in each hemisphere, but none in the equatorial plane, Fig. 28. The outer shell has twice the diameter of the inner one, so as to allow the same space for each cell. Each cell may hold two electrons, and in argon, the next member of the family to neon, has an atom like neon, but with a second layer of eight electrons, making 18 electrons in all. Outside this in the krypton atom is a concentric shell of 18 electrons, in the xenon atom there is a second layer of 18 electrons. Eight of the nine electrons in each hemisphere of krypton are placed symmetrically with respect to the polar axis and the electrons in the second shell; the ninth electron in each hemisphere goes to the polar axis. This also accounts for the position and properties of the iron family. In the niton atom there is a third shell with 32 electrons. The distribution of the electrons in the various shells is:

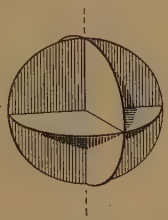

FIG. 27. — Outer Shell of Neon with Eight Cells.

FIG. 28.—Neon Atom.

		Layers of electrons.	Total electrons.
First shell		$2=2\times1^2$	2 Helium
Second shell	1st layer	$8=2\times2^2$	10 Neon
	2nd layer	$8=2\times2^2$	18 Argon
Third shell	1st layer	$18=2\times3^2$	36 Krypton
	2nd layer	$18=2\times3^2$	54 Xenon
Fourth shell		$32=2\times4^2$	86 Niton

The electrons in the different layers thus bear a simple relation to one another, $2(1+2^2+2^2+3^2+3^2+4^2)$. J. R. Rydberg arranged the atomic numbers of these elements in a similar series. The more or less concentric spherical shells have the same thickness so that their radii form an arithmetical series 1, 2, 3, 4; each shell is divided into cells of equal volume. The 1st shell has 2 cells; the second, 8; the third, 18; and the fourth, 32. The innermost cell has one electron per cell; the other cells may have as a maximum two electrons per cell. When two electrons occupy one cell, they are disposed at different distances from the centre of the atom. The inner cells must contain their maximum quota of electrons before the outer cells can contain any. In the outer shell, two electrons may occupy one cell provided all the other cells contain at least one electron. The arrangement of the electrons in the atoms of different elements is shown in Table V. Hydrogen has a single positive charge and a single electron. Its positive and negative poles form an electric doublet of high moment which tends to attract all other bodies, something like a small magnet. Thus at. hydrogen is strongly adsorbed by surfaces. By sharing their electrons, two hydrogen atoms can form a stable pair so that the atoms form diatomic molecules with a weak external field. As in G. N. Lewis' theory of cubical atoms, the chemical properties of lithium, beryllium, and boron are determined by their tendency to give up electrons, to form stable octets; while carbon, nitrogen, and fluorine *take up* electrons to form stable octets.

The theory explains the periodic properties of the elements including the eighth group and the rare earths; the magnetic properties of the elements; and the valency of polar and non-polar compounds. It is assumed that electrons contained in the same cell are nearly without effect on each other. But the electrons in the outside layer tend to line themselves up (in a radial direction) with those of the underlying shell because of a magnetic field probably always to be associated with electrons bound in atoms, as in Parsons' magneton theory. This attraction may be more or less counteracted by the electrostatic repulsion between the outside electrons and those in the underlying shell. The electrons in the outside layer also repel each other, and thus tend to distribute themselves among the available cells so as to be as far apart as possible. The actual positions of equilibrium depend on a

balance between these three sets of forces together with the attractive force exerted by the nucleus.

TABLE V.—I. LANGMUIR'S ARRANGEMENT OF THE ELECTRONS IN THE ATOMS OF THE ELEMENTS.

Layer.	Number of electrons in kernel.	Number of electrons in outside shell.										
I	—	0	1 H	2 He	3	4	5	6	7	8	9	10
IIi	2	He	Li	Be	B	C	N	O	F	Ne		
IIii	10	Ne	Na	Mg	Al	Si	P	S	Cl	A		
IIIi	18	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
IIIi		10	11	12	13	14	15	16	17	18		
		Niβ	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
		0	1	2	3	4	5	6	7	8	9	10
IIIii	36	Kr	Rb	Sr	Y	Zr	Cb	Mo	43	Ru	Rh	Pd
		10	11	12	13	14	15	16	17	18		
IIIii		Pdβ	Ag	Cd	In	Sn	Sb	Te	I	Xe		
		0	1	2	3	4	5	6	7	8	9	10
IVi	54	Xe	Cs	Ba	La	Ce	Pr	Nd	61	Sa	Eu	Gd
			11	12	13	14	15	16	17	18		
IVi			Tb	Ho	Dy	Er	Tm	Tm_2	Yb	Lu		
		14	15	16	17	18	19	20	21	22	23	24
IVi		Erβ	Tm	$Tm_2\beta$	Ybβ	Luβ	Ta	W	75	Os	Ir	Pt
			25	26	27	28	29	30	31	32		
IVi		Ptβ	Au	Hg	Tl	Pb	Bi	RaF	85	Nt		
		0	1	2	3	4	5	6				
IVii	86	Nt	87	Ra	Ac	Th	UX_2	U				

When the number of electrons in the outside layer is small, the magnetic attraction exerted by the electrons of the inner shells tends to predominate over the electrostatic repulsion, but when the atomic number and the number of electrons in the outside layer increase, the electrostatic forces gradually become the controlling factor. As a result, when there are few electrons in the outer layer these arrange themselves in the cells over those of the underlying shell, but where the outside layer begins to approach its full quota of electrons the cells over the underlying electrons tend to remain empty.

The properties of the atoms are determined by the number and arrangement of electrons in the outside layer and the ease with which they are able to revert to more stable forms by giving up or taking up electrons, or by sharing their outside electrons with atoms with which they combine. The tendencies to revert to the forms represented by the atoms of the inert gases are the strongest, but there are a few other forms of high symmetry such as those corresponding to certain possible

forms of nickel, palladium, erbium, and platinum atoms towards which atoms have a weaker tendency to revert (by giving up electrons only). The very stable arrangements of electrons corresponding to those of the inert gases are characterized by strong internal but unusually weak external fields of force. The magnetic and electrostatic forces are each very nearly internally balanced. The smaller the atomic number of the element the weaker are these external fields. The pair of electrons in the helium atom represents the most stable possible arrangement. A stable pair of this kind forms only under the direct influence of positive charges. The positive charges producing the stable pair in the order of their stability, may be : (*a*) The nucleus of any element ; (*b*) Two hydrogen nuclei ; (*c*) A hydrogen nucleus together with the kernel of an atom ; (*d*) Two atomic kernels. After the very stable pairs the next most stable arrangement of electrons is the group of eight such as forms the outside layer in atoms of neon and argon. We shall call this stable group of 8 electrons the " octet." Any atom up to argon having more than two positive charges in its kernel tends to take up electrons to form an octet. The greater the charge on the kernel the stronger is this tendency. In exceptional cases, the octet can form about a complex kernel, that is, about a structure containing the kernels of two atoms bound together by a pair of electrons. Two octets may hold 1, 2, or sometimes even 3 pairs of electrons in common. A stable pair and an octet may hold a pair of electrons in common. An octet may share an even number of its electrons with 1, 2, 3, or 4 other octets. No electrons can form parts of more than two octets.

The covalency of an atom is the number of pairs of electrons it shares with other atoms. If we represent by e the total number of available electrons in the outside shells of the atoms forming a given compound, and let n be the number of octets formed, holding p pairs of electrons in common, we see that, for every pair of electrons shared, there is a saving of $2p$ in the number of electrons needed to form octets. We have, therefore, $e=8n-2p$, or $p=\frac{1}{2}(8n-e)$. Of course, electrons held by a hydrogen nucleus in common with an octet must not be counted in reckoning the value of p, since they do not result in any saving in the numbers of electrons required to form octets. The two hydrogen nuclei of water always tend to hold pairs of electrons, but not octets, consequently n is unity for the oxygen atom. There are six available electrons in the oxygen atom, and two in the hydrogen atom, hence $e=8$, and p is zero. No electrons are therefore held in common between octets. The two hydrogen nuclei are held by electrostatic attraction on two pairs of the electrons forming the octet. The water molecule may, therefore, be pictured as a cube with two hydrogen nuclei hanging on to opposite edges. This structure indicates that water forms molecules in which the electrostatic forces are almost completely compensated internally. All the electrons form an octet, and hence the molecule should have a rather weak external field of force. Water should, therefore, be easily volatile and should not be a good conductor of electricity. But the lower symmetry of the molecule, as compared with the neon atom, shows that the b.p. should be much higher. In the formation of carbon dioxide and nitrous oxide, the black discs in Fig. 29 show those electrons which share equally a position in both octets when the atoms come together. There is a remarkable resemblance between the two, the stability and properties should therefore be similar. This deduction is confirmed by the comparison of the properties of the two compounds in Table VI. In addition, there are the two hydrates, $N_2O.6H_2O$, and $CO_2.6H_2O$; the heats of formation are respectively 14·9 and 15·0 Cals. per mol ; the surface tensions are the same at 12·2° and 9° respectively. The refractive indices are 1·193

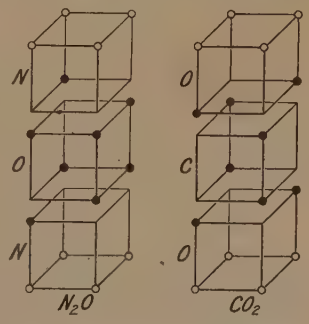

FIG. 29.—Formation of Molecules of Nitrous Oxide and Carbon Dioxide.

and 1·190; the dielectric constants, 1·598 and 1·582; the magnetic susceptibilities are the same, $0·12\times10^{-6}$; and the heat conductivity at 100° the same, 0·056. Carbon monoxide is regarded as an unsaturated compound, but it is really comparatively inactive. Its low b.p. shows that its external field is weak; and this corresponds with its low solubility. From the above formula, $n=2$, $e=10$, and $p=5$. This also suggests an unsaturated compound. Structurally it resembles nitrogen and the comparison of the properties of nitrogen and carbon monoxide. Table VI emphasizes the similarities. The resemblance in the mol. structure of

Table VI.—Comparison of the Properties of Carbon Dioxide and Nitrous Oxide; and of Nitrogen and Carbon Monoxide.

Property.	N_2O	CO_2	CO	N_2
Critical press.	75	77	35	35
Critical temp.	35·4°	31·9°	−151°	−146°
Critical vol.	—	—	5·05	5·17
Viscosity	148×10^{-6}	148×10^{-6}	163×10^{-6}	166×10^{-6}
Sp. gr. at −20°	0·996	1·031	—	—
Sp. gr. at 10°	0·856	0·856	—	—
Sp. gr. at b.p.	—	—	0·793	0·797
Solubility water at 0°	1·305	1·780	3·5	2·46
Solubility alcohol at 15°	3·25	3·13	—	—
F.p.	—	—	−207°	−213°
B.p.	—	—	−190°	−195°
Mol. number	22	22	14	14

carbon monoxide, nitrogen, N_2, and nitric oxide is emphasized by the diagrams, Fig. 30. Nitric oxide has 15 electrons—one more than nitrogen, N_2, or carbon monoxide. O. R. Foster described a number of atom models based on I. Langmuir's hypothesis.

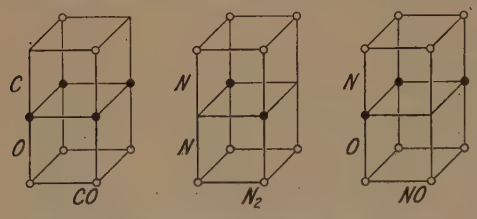

Fig. 30.—Molecular Structure of Carbon Monoxide, Nitrogen, and Nitric Oxide.

I. Langmuir applies the hypothesis to a great number of compounds—*e.g.* the phosphorus, acids, sulphur acids, nitrogen oxides, etc. In many compounds, the co-ordination number and the covalence are identical, and the octet theory then corresponds exactly to A. Werner's theory, just as for organic compounds it is eq. to the ordinary valency theory. In hydrofluoroboric acid, HBF_4, $n=5$, $e=32$, $p=4$; each fluorine atom thus shares a pair of electrons with the octet of the boron atom—the covalence is 4. In ammonium fluoride, $n=2$, $e=16$, and $p=0$; the four hydrogen nuclei thus attach themselves to the nitrogen octet giving rise to the positive ion $NH_4^{\cdot}$, and since chlorine has a complete octet it becomes a negative Cl'-ion. Hence, ammonium chloride resembles a sodium chloride, the central nitrogen atom has a covalence of 4. In platinous tetramminodichloride, $n=7$, $e=48$, $p=4$. Four NH_3-radicles are thus attached directly to the platinum, each sharing a pair of electrons; the nitrogen and platinum have each a covalence of four, and the chlorine atoms become ions.

Compounds having the same number of atoms, and the same total number of electrons arranged in a similar manner, are said to be **isosteric compounds**—ἴσος, equal; στερεός, solid—*e.g.* nitrous oxide and carbon dioxide. The essential differences between isosteric molecules are confined to charges on the nuclei of the constituent atoms. Electrically charged groups of atoms or even single atoms may be isosteric:

Type 1, H', He, $Li^{\cdot}$; type 2, O'', F', Ne, $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$; type 3, S'', Cl', A, $K^{\cdot}$, $Ca^{\cdot\cdot}$; type 4, $Cu^{\cdot}$, $Zn^{\cdot\cdot}$; type 5, Br', Kr, $Rb^{\cdot}$, $Sr^{\cdot\cdot}$; type 6, $Ag^{\cdot}$, $Cd^{\cdot\cdot}$; type 7, I', Xe, $Cs^{\cdot}$, $Ba^{\cdot\cdot}$;

type 8, N_2, CO, CN'; type 9, CH_4, NH_4'; type 10, CO_2, N_2O, N_3', CNO'; type 11, NO_3', CO_3''; type 12, NO_2', O_3; type 13, HF, OH'; type 14, ClO_4', SO_4'', PO_4'''; type 15, ClO_3', SO_3'', PO_3'''; type 16, PO_3'; type 17, S_2O_6'', P_2O_6''''; type 18, S_2O_6', P_2O_7''''; type 19, SiH_4, PH_4^+; type 20, MnO_4', CrO_4''; type 21, SeO_4'', AsO_4'''.

Where isosteric groups or molecules have the same charges, they are **isoelectric,** and their properties are comparable—*e.g.* N_2 and CO—but when the charges are unlike, the resemblance may show itself as a similarity in crystalline forms.

The following cases of crystalline isomorphism are thus predicted by the theory and are found to exist according to published crystallographic data: $NaF—MgO$; $KNO_2—KNCO$; $KNO_3—SrCO_3$; $KClO_4—SrSO_4$; $NaHSO_4—CaHPO_4$; $MnSeO_4.H_2O—FeAsO_4.2H_2O$, etc. The following cases are predicted by the theory, but cannot yet be tested because of lack of available data: $MgF_2—Na_2O$; $K_2S—CaCl_2$; $NaClO_3—CaSO_3$; $KHSO_3—SrHPO_3$; $Na_2S_2O_6—Ca_2P_2O_6$; $Na_2S_2O_7—Ca_2P_2O_7$; etc. Carbonates and sulphites are not isomorphous, the covalence of the central atom being 4 and 3 respectively. Nitrates and chlorates are not isomorphous, the covalency of the chlorine being 3 in chlorates. There are some disagreements—*vide* the plagioclases.

G. N. Lewis' and I. Langmuir's theory or analogous theories have been discussed by S. C. Bradford, A. E. Oxley, W. M. Latimer and W. H. Rodebush, E. C. Kemble, N. R. Campbell, H. Tertsch, A. W. Stewart, C. Schmidt, H. Teudt, R. N. Pease, F. Hocheder, E. Neusser, O. Hinsberg, A. C. Crehore, E. D. Eastman, H. S. King, G. A. Perkins, H. I. Cole, J. A. Wasastjerna, J. Steiglitz, J. Moir, D. L. Webster and L. Page, R. G. W. Norrish, C. R. Bury, etc. A. O. Rankine showed that the viscosity data and X-ray crystal data are consistent with G. N. Lewis' and I. Langmuir's hypothesis; but J. R. Partington stated that the hypothesis is inconsistent with the sp. ht. of the gases. For example, the ratio of the two sp. ht. of a rigid molecule with three atoms in line should be 1·400, whereas the ratio of the two sp. ht. of carbon dioxide or nitrous oxide is 1·3. Similarly, for the rigid nitrogen molecule the ratio should be 1·667 instead of 1·400 actually observed. In consequence, A. W. C. Menzies has shown that supplementary hypotheses are necessary.

This discussion has not proved these speculations, it only makes them appear plausible; and it illustrates the invaluable aid which chemistry and meta-chemistry are receiving from the exercise of disciplined imagination. Naturally many have fallen before the temptation to confuse imaginary phenomena with demonstrated fact. Premature generalizations are rife, since, as a rule, the less the number of facts, the easier it is to generalize—and the more likely are those generalizations to be wrong. J. J. Thomson said:

> The theory is not an ultimate one; its object is physical rather than metaphysical. From the point of view of the physicist, a theory of matter is a policy rather than a creed. Its object is to connect or co-ordinate apparently diverse phenomena, and, above all, to suggest, stimulate, and direct experiment. It ought to furnish a compass which, if followed will lead the explorer further and further into unexplored regions. Whether these regions will be barren or fertile, experience alone will decide; but at any rate, one who is guided in this way will travel onward in a definite direction and will not wander aimlessly to and fro.

The honesty of science.—Here, then, we are confronted with phantasmæ which would be banished at once if we were convinced that they were sterile conjectures and not pregnant hypotheses. The speculations probably make the best guess yet made about the ultimate constitution of matter. The relations between hypotheses and fact, though doubtful, are not altogether contradictory. Consequently, the defective hypotheses will be persistently attacked by hostile forces until they are either abandoned in favour of more successful rivals, or developed and strengthened into a more consistent and lasting form.

This struggle for existence is the life and strength of scientific hypotheses. Science may appear to lose influence when the fallacy of a prevailing hypothesis is demonstrated; but it holds a treasured reputation for honesty of purpose by frankly acknowledging and registering its mistakes. In the words of A. Sidgwick,

free from the fear of being found an impostor, science is able to challenge and to court correction. "As for the truth, it endureth, and is always strong; it liveth and conquereth for evermore. Truth is the strength, the kingdom, the power, and the majesty of all ages."—1 Esdras iv, 38.

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CHAPTER XXVIII

BERYLLIUM OR GLUCINUM

§ 1. The Discovery and Occurrence of Beryllium or Glucinum

C'est à la géométrie que l'on doit en quelque sorte la source de cette découverte (de cet élément) ; c'est elle qui en fournit la première idée, et l'on peut dire que sans elle la connaissance de cette terre nouvelle n'eût point été acquise de longtemps, puisque, d'après l'analyse de l'émeraude par M. Klaproth, et celle du béril par M. Bindheim, on n'aurait pas cru devoir recommencer ce travail sans les fortes analogies ou même l'identité presque parfaite que le citoyen Haüy avait trouvées par les propriétés géométriques entre ces deux fossiles pierreux.—A. F. DE FOURCROY.

THE mineral **beryl** occurs in hexagonal crystals which are variously coloured white, yellow, blue, or pale rose-red, but more commonly green—the pale green varieties are known as *aquamarine*, and the dark green varieties, as *emerald*, which is familiar as a gem-stone. The so-called *golden beryl* is bright yellow. The beryls are all more or less impure forms of beryllium aluminosilicate, $3BeO.Al_2O_3.6SiO_2$; the rich green colour is due to chromium. The minerals *davidsonite*, *goschenite*, *rosterite*, and *vorobyevite* are also varieties of beryl. The *smaragd*, σμάραγδος, and the beryl, βήρυλλος, were known to the ancients as ornamental gem-stones ; they are frequently mentioned in the Bible, and we are there told that the smaragd, or *emerald*, was assigned the fourth place in the breastplate of the high-priest of the tabernacle. Theophrastus, in his Περὶ Λίθος, about the third century B.C., wrote about the smaragd, and it is generally assumed that his description refers to our emerald. Although it is obvious that Theophrastus, and later, Pliny in his *Historia Naturalis*, written about the middle of the first century of our era, applied the term smaragd to many other minerals besides the emerald proper, Pliny said of one variety :

There is no stone more pleasing to the eye, for whereas the sight fixes itself with avidity upon the green grass, and the foliage of trees, we have all the more pleasure in looking upon the *smaragdus*, for there is no green in existence of a more intense colour than this ; and besides, of all the precious stones, this is the only one that feeds the sight without satiation. Even when the vision has been fatigued, with intently viewing other objects, it is refreshed by being turned upon this stone ; and lapidaries know of nothing that is more soothing to the eyes, for its soft green tints are wonderfully adapted for assuaging lassitude, when felt in those organs.

Pliny also referred to *beryllus* as having a like nature to that of the emerald. D. A. MacAlister[1] has described the locality known as Cleopatra's Emerald Mines of Jebel Sikait, Etbai, which have been worked over 2000 years. A. B. de Boot applied the name *aquamarine* to a sea-green coloured variety. From the old analyses of T. Bergman,[2] F. C. Achard, J. J. Bindheim, M. H. Klaproth, and L. N. Vauquelin, beryl was regarded as a calcium aluminium silicate ; while beryl and smaragd were regarded as two distinct mineral species. R. J. Haüy first suspected the identity of emerald and beryl from the sameness of their crystallographic and other physical characteristics, and he therefore invited L. N. Vauquelin [3] to analyze these minerals ; and as a result, the latter opened his memoir : *De l'aigue marine ou béril, et découverte d'une terre nouvelle dans cette pierre*, with these words :

Le citoyen Haüy, dit-il dans son mémoire lu à l'Institut le 26 pluviose an VI, ayant trouvé une conformité parfaite entre la structure, la dureté et la pesanteur du béril et de

l'émeraude, m'engagea, il y a quelques mois, à comparer aussi ces deux pierres par les moyens chimiques, pour savoir si elles étaient composées de mêmes principes et dans les proportions semblables.

L. N. Vauquelin found that *la terre du béril*, as he called it, can be separated from aluminium by boiling the soln. with potassium hydroxide; and it differs from aluminium in furnishing salts with a sweet taste, in forming no alum, in being soluble in ammonium carbonate, and in not being precipitated by potassium oxalate or tartrate. The editors of the *Annales de Chimie*, in which Vauquelin's paper was published, suggested the name *glucine* from γλυχύς, sweet, in reference to the sweet taste of the salts. L. N. Vauquelin adopted this term with some reluctance; he referred, in a footnote, to the proposed name *glucine*, and later still, he employed this term—possibly because of some pressure from the editors of the *Annales*. H. F. Link objected to the use of the proposed name on account of its resemblance to "glycine," already in use for something else. M. H. Klaproth added that the sweetness of the salts of *la terre nouvelle* is not unique with that element, for the salts of yttria are also sweet, and he claimed that *Beryllerde* is a preferable term. A. G. Ekeberg agreed with M. H. Klaproth; and J. F. Gmelin translated the French *glucine* into the German equivalent *Susserde*. Thereafter, the term *Beryllerde*, obviously translated from L. N. Vauquelin's *la terre du béril*, was employed in Germany, and *glucine* in France. F. Wöhler employed the term *beryllium* for the metal which he isolated in 1828. In other countries there has been a kind of struggle for existence between the terms *beryllium* and *glucinum*, and neither designation has yet ousted the other. In 1905, J. L. Howe argued in favour of the latter, C. L. Parsons in favour of the former, and this is emphasized in the monograph: C. L. Parsons, *The Chemistry and Literature of Beryllium* (Easton, Pa., 1908). Argument is of no avail because the choice of terms is largely a question of temperament.

T. Richardson [4] reported that the Aberdeen mineral, davidsonite, contained a new element which he called *donium*; and H. S. Boase, an element *treenium*. M. F. Heddle identified donium with beryllium.

Numerous analyses [5] of the different varieties of **beryl** have been reported in addition to those to which allusion has been made. Some gigantic beryls have been reported in the United States—one found at Grafton (New Hampshire) is said to have weighed 2900 lbs., and another from the same locality, 1076 lbs. Other deposits are at Ackworth (New Hampshire), Royalston (Massachusetts), Albany (Maine), Haddom (Connecticut), Lieperville and Chester (Pennsylvania), Stony Point (North Carolina), Amelia Court House (Virginia), Coosa County (Alabama), Black Hills (Dakota), and in Chaffee County and Jefferson County (Colorado). Beryls are found in Cornwall (England), Kinloch Rannoch, Braemar, and Cairngorm (Scotland); several places in Ireland; Limoges (France); Finbo and Broddbo (Sweden); Bodenmais and Rabenstein (Bavaria); Elba; East Indies; etc. Beryl usually contains between 9 and 16 per cent. of beryllia; up to about 2 per cent. of lithia has been reported in numerous samples; W. Vernadsky's analyses showed the presence of up to 3·6 per cent. of cæsia, and 1·3 per cent. of rubidia. W. A. Tilden found that up to about 6·7 vols. of gas were evolved when beryl was heated, and most of this was carbon dioxide. R. J. Strutt, and A. Piutti have measured the helium which can be driven from beryl.

The beryllium hydro-aluminosilicate, $BeHAlSiO_5$, occurs as the mineral **euclase** in Brazil, South Urals, and the Austrian Alps. This rare mineral was analyzed by J. J. Berzelius,[6] J. W. Mallet, and A. Damour. These analyses show 16·97 to 21·78 per cent. of beryllia. Beryllium occurring as a simple silicate, Be_2SiO_4, is represented by the mineral **phenacite** with from 44·46 per cent. of beryllia,[7] which was named from φέναξ, a deceiver, on account of its resemblance to quartz. It is found at Mount Antero (Colorado), at Framont (Vosges), in the emerald mines of the Urals, etc. It is also found in the mineral **bertrandite**, beryllium hydrosilicate, which approximates in composition, $Be_2(BeOH)_2Si_2O_7$, it has 40–43 per cent. of beryllia. Phenacite is found at Barbin (Nantes), Pisek (Bohemia), Mount Antero (Colorado), and at Stoneham (Maine).[8] The analyses of the silicate minerals

leucophane, $Na(Be,F)Ca(SiO_3)_2$, by H. Erdmann,[9] C. F. Rammelsberg, and W. C. Brögger; and of **meliphane**, or **melinophane**, or **meliphanite**, $NaCa_2Be_2FSi_3O_{10}$, by R. Richter, C. F. Rammelsberg, and W. C. Brögger, show the presence of 10–14 per cent. of beryllia; **eudidymite**, analyzed by W. C. Brögger, and A. E. Nördenskjöld, and **epididymite**, $HNaBeSi_3O_8$, of 10–13 per cent. of beryllia; **gadolinite**, $FeBe_2Y_2Si_2O_{10}$, analyzed by G. Flink,[10] show 5–11 per cent. of beryllia; **trimerite**, $Be(Mn,Ca,Fe)SiO_4$, analyzed by G. Flink, 16–17 per cent.; **cyrtolite** and **alvite** show 14–15 per cent.; **allanite**, up to about 0·3 per cent.; **muromonite**, 5–6 per cent.; **erdmannite**, up to 4 per cent.; **foresite** and **arrhenite**, up to 1 per cent.; and **bityite**, up to 2 per cent. of beryllia. The two minerals: **danalite**, $(Be,Fe,Zn,Mn)_7Si_3O_{12}S$, and **helvite**, $(Be,Fe,Mn)_7Si_3O_{12}S$, have 13–14 per cent. of beryllia.

Beryllium aluminate, $Be(AlO_2)_2$, is represented by the mineral **chrysoberyl**, with 19–20 per cent. of beryllia found in river gravels along with beryl and phenacite in mica schists, etc., in Brazil, Ceylon, Urals, Orange County (U.S.A.), etc. It is generally a pale yellowish-green, and is principally used as a gem-stone; the dark green crystals from the Urals are called **alexandrite**. The crystals exhibit a peculiar dichroism, being leek-green or emerald-green by reflected light, and deep raspberry-red or violet in transmitted light. They also appear red in gaslight, and green in daylight. The chatoyant bluish-white opalescent variety from Ceylon is known as *cat's-eye*, and the variety with a wavy opalescence, **cymophane**—from *κῦμα*, a wave. Sodium beryllium phosphate, $NaBePO_4$, is represented by **beryllonite**, from Maine; it has 19–20 per cent. of beryllia; calcium beryllium fluophosphate, $BeCaFPO_4$, is represented by the gem-stone **herderite**, or **allogonite**, from Maine and Saxony; it has 15–16 per cent. of beryllia; the rare **hamlinite**, or **bowmanite**, which occurs with herderite and bertrandite, is a beryllium aluminium hydrofluophosphate. The native basic borate **hambergite**, $BeOH.BeBO_3$, contains about 53 per cent. of beryllium oxide; and the aluminoborate, **rhodizite**, contains about 10 per cent. of beryllium oxide. J. W. Mallet [11] found the Virginian tantalo-niobate, *sipylite*, had 0·62 per cent. of beryllia. The complex carbonate, *tengerite*, may carry up to 9–10 per cent. of beryllia.

Beryllium is not very abundantly distributed in nature, but small quantities are found in a great many minerals; and if it had been specially sought in the more frequent mineral and rock analyses, or if some simple method of separating it from aluminium had been known earlier, it is probable that the reports of its occurrence in small quantities would be much more extensive. The beryllium minerals usually occur in granitic rocks. Beryllium has also been found in the zirconium minerals *alvite* and *cyrtolite*. O. Boudouard reported traces of beryllia in monazite sands, T. L. Phipson reported 0·33 per cent. in some aluminous schists. A. Bécamp found a trace of beryllia in the sulphur waters in the district of Alais. J. N. Lockyer found lines corresponding with beryllium in the spectrum of the sun; M. Pomier in the waters of Antiveille (Basses-Pyrénées); and M. Mazade, in the waters of Nérac.

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§ 2. The Extraction of Beryllia

Beryllium is usually derived from beryl. Although there are minerals richer in this element, they are scarce and costly. G. Krüss and H. Moraht [1] treated finely powdered leucophane, suspended in water, with conc. sulphuric acid, and separated the beryllium from the resulting soln. as described below. C. James and G. A. Perley also digested gadolinite in conc. sulphuric acid. Beryl, however, is usually the cheapest and most convenient source of beryllium. The metal is not usually extracted directly, but is separated from the silica, alumina, etc., as oxide or a convenient salt. P. Lebeau's process is perhaps the most direct one yet proposed. He heated a mixture of beryl with half its weight of calcium carbide in an electric arc-furnace, and washed out the by-products with a mixture of hydrofluoric and sulphuric acids, and there remained 90–95 per cent. of the theoretical yield of beryllium. Reduction with carbon alone was not so satisfactory. Much of the silica volatilizes when beryl is heated in the electric arc-furnace.

In H. Debray's process, briquettes were made from a mixture of powdered beryl, carbon, and oil, and heated in a stream of chlorine, when carbon dioxide, silicon tetrafluoride, and iron, aluminium, and beryllium chlorides were evolved. C. A. Joy tried the process but did not recommend it. Powdered beryl is not

attacked by any single acid, excepting hydrofluoric acid. The mineral is usually heated with a flux—alkali hydroxides, alkali carbonates, calcium or potassium fluoride, or ammonium fluoride—in order to get the mineral in a form readily attacked by acids so as to get the beryllium all in soln. C. A. Joy tried many of these methods of breaking up the mineral. The fluoride fluxes have the advantage of readily removing the excess of silica as silicon tetrafluoride, and C. A. Joy found that the treatment with potassium fluoride and sulphuric acid is an excellent method except for the cost of the acid, to which might be added the high cost of platinum vessels. With the calcium fluoride processes, the large amount of calcium compounds introduced complications. L. N. Vauquelin, G. Wyrouboff, J. H. Pollok, and C. L. Parsons and S. K. Barnes used alkali hydroxide; H. N. Warren, sodium carbonate; H. Debray, quicklime; J. Gibson, ammonium hydrofluoride; W. Gibbs, potassium hydrofluoride; G. Scheffer, a mixture of calcium fluoride and sulphuric acid; and P. Lebeau, calcium fluoride in a graphite crucible in an electric furnace. L. Burgess heated the ore with carbon, and volatilized the beryllium as chloride by treating the product with hydrogen chloride; H. S. Booth and G. G. Marshall heated a mixture of the crushed ore with an alkali earth halide at a temp. at which beryllium halide is formed.

P. Berthier heated an intimate mixture of powdered beryl and marble in a high temp. furnace; H. Debray used a mixture of beryl and calcium oxide, which virtually amounts to the same thing. C. A. Joy found the crucible was not so much attacked if calcium sulphate is also included in the mixture. The resulting glass is decomposed by nitric acid. C. A. Joy also tried fusion with litharge, followed by treatment with nitric acid, and fusion with manganese dioxide followed by treatment with sulphuric acid; but he did not recommend any of these processes.

According to C. A. Joy,[2] the best results are obtained by fusing an intimate mixture of powdered beryl with twice its weight of potassium carbonate. H. N. Warren used sodium carbonate as a flux; and C. A. Joy tried a mixture of sodium and potassium carbonates. An essentially similar method of opening up beryl was employed by G. Klatzo, L. F. Nilson and O. Pettersson, E. Hart, C. L. Parsons, etc. L. N. Vauquelin fused the powdered mineral with three times its weight of potassium hydroxide; G. Wyrouboff, and C. L. Parsons recommended the same opening agent. A silver, nickel, or iron crucible can be used. The powdered mineral is fused with sodium carbonate in a fireclay crucible and the molten mass poured out to cool on an iron plate. The powdered mass is washed with water to remove soluble alkali salts—a little beryllium is lost at the same time. The residue is treated with an excess of sulphuric acid. The soln. is evaporated and heated on a sand-bath until the acid begins to fume. The cold residue is extracted with hot water, and the insoluble silica rejected. The mother liquid is evaporated until alum begins to crystallize from the soln.; on standing, a large proportion of the aluminium separates as potash alum. Beryllium forms no alum. The iron in soln. is oxidized with a little potassium chlorate or nitric acid. A mixture of aluminium, ferric, and beryllium hydroxides is then precipitated by adding a slight excess of ammonia. Several methods are now available for separating the alumina and beryllia. H. T. S. Britton found a 90 per cent. separation of alumina and beryllia is possible by a crystallization of the former as potassium alum.

According to H. Copaux's method of separation, the finely powdered mineral is heated at 850° for half an hour with twice its weight of sodium fluosilicate. The product, which consists of silica and the double fluorides of sodium and aluminium and sodium and beryllium, is extracted three times with boiling water. The extract is filtered, and to the filtrate boiling aq. sodium hydroxide is added in slight excess. The oxide of beryllium precipitated, along with a little alumina and silica, is dissolved in sulphuric acid, and beryllium sulphate crystallizes out on concentrating the soln. In this way 90 per cent. of the beryllium in the beryl is recovered. For the estimation of beryllium in beryl, 5 grms. of the powdered mineral are treated as above with 20 grms. of sodium fluosilicate. The precipitation with sodium hydroxide is omitted and an aliquot portion (300 c.c. out of 1 litre) of the filtered aq. extract is evaporated with sulphuric acid until white fumes appear. The residue is treated with water, and an excess of ammonia is added. If the precipitate contains a

noticeable quantity of iron it is redissolved in acetic acid and the iron removed by means of nitroso-β-naphthol. The filtrate is boiled and made alkaline with ammonia, and the precipitate is filtered off, dried, ignited, and weighed. Any silica present is removed by treatment with hydrogen fluoride, and the aluminium and beryllium are separated by fusion with sodium carbonate, etc.

(1) L. N. Vauquelin [3] found that while ammonium carbonate precipitates both metals as hydroxides or carbonates, the beryllia alone dissolves in an excess of that reagent. A. Zimmermann showed that the presence of ammonium chloride favours the separation. This reaction has been studied by C. A. Joy, G. Scheffer, A. Hofmeister, F. Toczyknsky, etc. T. Scheerer showed that the small quantity of iron dissolved by the ammonium carbonate soln. can be precipitated by ammonium sulphide. (2) J. J. Berzelius, and H. Rose found that with a boiling soln. of an ammonium salt, beryllia goes into soln. while alumina remains insoluble. This reaction has been studied by A. Hofmeister, E. Hart, and J. Weeren. (3) C. Renz noted that both aluminium and beryllium are precipitated by methyl- or ethyl-amine, but alumina is alone dissolved by an excess of the precipitant, the beryllia remaining insoluble. In 1880, C. Vincent recommended dimethylamine for the same purpose. (4) C. Rössler found that in the presence of citric acid, beryllia is alone precipitated by ammonium phosphate. (5) According to H. Rose, (*a*) tartaric acid, and other organic acids which retard the precipitation of iron and aluminium hydroxides, have no influence on the beryllium salt; (*b*) a boiling soln. of sodium acetate precipitates alumina but not beryllia; (*c*) barium carbonate precipitates alumina from a neutral soln., while the beryllia remains dissolved. (6) L. N. Vauquelin, C. G. Gmelin, and F. Schaffgotsch showed that a cold soln. of potassium hydroxide dissolves both alumina and beryllia; the former remains dissolved when the soln. is boiled, and the beryllia is precipitated. The reaction was studied by C. A. Joy, J. Weeren, and L. A. Aars. (7) P. Berthier found that sulphurous acid or ammonium sulphite dissolves the hydroxides of both metals in the cold, but when the soln. is heated, alumina is precipitated while the beryllia remains in soln. H. Böttinger showed that the method is unsatisfactory, though B. Glassmann rediscovered the discarded process. (8) C. A. Joy found alumina is alone precipitated by boiling a neutral soln. of alumina and beryllia with sodium thiosulphate, but the results were poor. (9) F. S. Havens found that aluminium chloride is not soluble in a soln. of hydrogen chloride in dried ether, while beryllium chloride dissolves therein. J. H. Pollok showed that the ether can be omitted, and the aq. soln. sat. with hydrogen chloride. (10) According to H. D. Minnig, a soln. of acetyl chloride in acetone precipitates aluminium chloride as $AlCl_3.6H_2O$, while iron and beryllium chlorides remain in soln. (11) F. Haber and G. van Oordt dissolved basic beryllium acetate in chloroform, leaving the acetates of iron and aluminium undissolved. (12) C. L. Parsons and W. O. Robinson separated basic beryllium acetate from the other acetates by means of its ready solubility in hot glacial acetic acid, and its insolubility in that reagent when cold. (13) C. L. Parsons and S. K. Barnes separated beryllium hydroxide by virtue of its solubility in a sat. soln. of sodium hydrogen carbonate, and the insolubility of iron and aluminium hydroxides in the same menstruum. The reaction was studied by F. Brau and G. van Oordt. (14) W. Gibbs suggested the use of sodium fluoride to separate quantitatively alumina and beryllia, and J. H. Pollok showed that the separation is exceedingly sharp. (15) L. E. Rivot proposed to separate iron from alumina and beryllia by reducing the iron oxide by heating the mixed oxides in a stream of hydrogen and dissolving out the metal with dil. nitric acid; J. P. Cooke proposed to volatilize the reduced iron in a stream of hydrogen chloride, and F. S. Havens and A. F. Way showed that the preliminary reduction by hydrogen is not necessary. (16) M. Schleir, E. A. Atkinson and E. F. Smith, and R. Burgass showed that iron can be quantitatively separated from beryllium by means of nitroso-β-naphthol. (17) P. Lebeau precipitated the iron in a nitric acid soln. with potassium ferrocyanide, the excess of ferrocyanide with copper nitrate, and the excess of copper with hydrogen sulphide. (18) H. Debray developed a separation dependent on the action of zinc on the mixed sulphates precipitating the aluminium as a basic sulphate. The reaction was studied by G. Scheffer. (19) E. Hart separated most of the iron and aluminium from the beryllium by the fractional precipitation with sodium carbonate; the great solubility of beryllia in a soln. of its own sulphate causes it to be the last to precipitate. (20) G. Wyrouboff precipitates beryllium from its soln. in hydrochloric acid as a double oxalate with potassium; the aluminium and iron remain in soln. (21) According to P. E. Browning and S. B. Kuzirian, beryllium and aluminium nitrates are dissolved in a little water and boiled with amyl alcohol until the water has all evaporated; the beryllium nitrate dissolves, the aluminium nitrate remains insoluble. (22) By heating the mixed acetates to 160°–170°, at 19 mm. press., beryllium acetate sublimes, iron and aluminium acetates do not. (23) According to G. van Oordt, aged beryllium hydroxide becomes insoluble in dil. soln. of acids and alkalies so that iron oxides can be extracted by the former, and alumina by the latter. (24) M. Wunder and P. Wenger fused the mixture of beryllia, iron oxide, alumina, and chromic oxide with sodium carbonate for 2–3 hrs. When the cold mass is extracted with water, the aluminium and chromic oxides pass into soln. The iron and beryllium oxides can then be separated by fusion with potassium hydrosulphate; and the iron precipitated from the aq. soln. of the cold cake by potassium hydroxide; and the filtrate, acidified, is treated with aq. ammonia when beryllia is precipitated. (25) G. Wyrouboff found that the

double oxalate $2BeC_2O_4.3K_2C_2O_4$ is only sparingly soluble, while the double oxalates of iron, aluminium, and chromium are nearly twice as soluble. (26) A. Classen electrolyzed an ammonium oxalate soln. of iron, aluminium, and beryllium; the current can be regulated so that the iron is reduced, and the aluminium precipitated as hydroxide by the ammonium carbonate produced while the beryllium remains in soln. (27) R. E. Myers precipitated iron in a mercury cathode by the electrolysis of a mixed slightly acid soln. of the sulphates of iron and beryllium.

The procedure recommended by C. L. Parsons is to saturate the neutral soln. of aluminium, iron, and beryllium salts with crystals of sodium hydrocarbonate; warm the liquid for 24 hrs., and to shake frequently. Most of the beryllium passes into soln., while the iron and aluminium are precipitated—completely if other salts be not present. By dissolving the residue left after filtration and repeating the treatment, practically all the beryllium will be found in the hydrocarbonate soln. Add ammonium sulphide to remove any dissolved iron, and dil. the soln. to five times its original volume. By blowing steam through the soln. until it has reached its b.p., the beryllium will be all precipitated as a granular basic carbonate easily washed. The precipitate has about 2 per cent. of occluded alkali which can be removed by re-solution in acid, followed by precipitation of beryllium hydroxide with ammonia.

To get rid of any rare earths, if such be present, G. Krüss and H. Moraht dissolved the beryllia in hydrochloric acid, neutralized with ammonia, added an excess of ammonium oxalate, and then sufficient dil. hydrochloric acid to dissolve the flocculent precipitate of beryllium oxalate. The oxalates of the rare earths remain insoluble. The soln. can be dropped into one of ammonium carbonate containing an excess of ammonia and ammonium oxalate and the filtrate treated with steam for the precipitation of basic beryllium carbonate. The hydroxide or basic carbonate can be used as a starting-point for the preparation of other beryllium compounds.

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§ 3. The Preparation and Properties of Beryllium

About ten years after L. N. Vauquelin's discovery of beryllia, H. Davy [1] tried to reduce this oxide (*a*) by fusing it in a clay crucible with iron filings and potassium, obtaining a semi-malleable metallic mass which was harder and whiter than iron; and (*b*) by heating it in a platinum tube in the vapour of potassium. He obtained a pyrophoric dark grey mass containing "small metallic particles which were as soft as potassium, but so small that they could not be more minutely examined, as they melted in boiling naphtha." It is thus very uncertain whether H. Davy succeeded in isolating the metal beryllium. In 1812, F. Stromeyer also claimed to have succeeded in alloying the metal with iron by melting in a closed crucible a mixture of beryllia, carbon, and iron made into a paste with linseed oil. It is doubtful if F. Stromeyer's claim was justified by the results. H. N. Warren claimed to have reduced beryllia in a stream of hydrogen in thin tubes of lime, heated by the oxy-hydrogen flame.

The preparation of beryllium by reduction with metals.—F. Wöhler reduced beryllium chloride with potassium in a platinum crucible, and for the first time obtained the metal, which he called beryllium, as a dark grey powder. Shortly afterwards, and independently, A. A. B. Bussy prepared the metal, which he called glucinum, by a process similar to that employed by F. Wöhler. H. Debray substituted sodium for potassium, and passed the vapour of beryllium chloride over the molten metal; and in 1867, M. Ménier exhibited a sample of beryllium at the Paris Exhibition; he prepared it by the action of sodium on a mixture of beryllium chloride, and the double fluoride of beryllium and potassium, heated in an aluminium crucible. J. E. Reynolds, and L. F. Nilson and O. Pettersson reduced the chloride with sodium; and T. S. Humpidge obtained a metal of 99·2 per cent. purity by this means. J. H. Pollok also produced the metal by reducing the chloride with sodium, but he was unable to fuse together the dark grey powder, because, said he, the metal probably volatilizes without passing through the liquid state. M. A. Hunter heated the chloride in a bomb with sodium. G. Krüss and H. Moraht reduced the double fluoride of beryllium and potassium by sodium, and obtained the metal in hexagonal plates. C. Winkler claimed to have reduced the oxide by magnesium, and H. Goldschmidt, by aluminium, but both methods are unsatisfactory. G. Krüss and H. Moraht used an excess of magnesium and freed the beryllium from magnesium and magnesia by boiling the product for a long time with a soln. of ammonium chloride. K. A. Kühne proposed to use the chlorates or perchlorates in the mixture with H. Goldschmidt's process.

The preparation of beryllium by electrolytic processes.—H. Davy heated an iron wire to whiteness by a battery of 1000 plates, and while negatively electrified fused it in contact with beryllia slightly moistened, and in an atm. of hydrogen gas. He thus obtained an alloy of iron and beryllium. In 1831, A. C. Becquerel thought he had reduced a soln. of beryllium chloride mixed with a little ferric chloride to make it conducting; and, in 1895, H. N. Warren stated that he obtained the metal by the electrolytic reduction of the bromide, with a current of 12 volts and 8 amps.—but the bromide is a non-conductor. In the same year, W. Borchers proposed to

electrolyze a molten mixture of beryllium chloride and an alkali chloride or an alkaline earth chloride. The mixture was made by evaporating a soln. of the two chlorides mixed with a little ammonium chloride to arrest hydrolysis. Calcium and magnesium chlorides should be absent. No statement of the results was made. L. F. Nilson and O. Pettersson electrolyzed a conc. soln. of the chloride with a mercury cathode but obtained no amalgam. P. Lebeau proved that the molten beryllium halides do not conduct electricity, but in the presence of an alkali fluoride, the soln. readily conducts the current; he developed a simple and easy process for producing the metal almost free from foreign admixtures, by electrolyzing the molten double fluoride of beryllium and sodium (or potassium), $BeF_2.NaF$, in a nickel crucible heated over a Bunsen's burner. The salt was made by fusing eq. amounts of the component fluorides. F. Fichter and E. Brunner have emphasized the need for thoroughly dehydrating the mixed fluorides by fusion to a clear glass and removing the scum, before the electrolysis. A current of 6–9 amps. and 35–40 volts was passed and the source of heat removed. The nickel crucible served as negative pole, and a graphite rod as positive pole. During the electrolysis, the heat was maintained just a little above the m.p. of the salt; and the metal was obtained in hexagonal crystals. According to F. Fichter and K. Jablczynsky, if the temp. of the bath rises too high, an alloy of nickel and beryllium is formed. The metal is isolated from the fused mass by dissolving the salts in water, and the soln. is prevented from becoming acid by the addition of ammonia, and the repeated renewal of the water. The crystals of beryllium are freed from admixed oxide by centrifuging in a mixture of ethylene dibromide and alcohol—sp. gr. 1·95. The small crystals so obtained cannot be melted together under ordinary conditions owing to the coating of oxide preventing coalescence; it is necessary to form cylinders by compression, and then heat them up in an electric vacuum furnace, or in one containing hydrogen at 11–15 mm. P. H. M. P. Brinton used a similar process. F. Fichter and E. Brunner used a tungsten tube vacuum furnace. By a similar method of preparation G. Oesterheld obtained a metal with 99·5 per cent. beryllium, and stated that the principal impurity is beryllium carbide. A. Stock and H. Goldschmidt made the compact metal by the electrolysis of a fused bath of an alkaline earth fluoride containing a beryllium compound.

R. Grätzel electrolyzed a molten soln. of the oxide in the chloride of an electropositive metal—say calcium. He assumed that the calcium liberated at the cathode reacted with the beryllia in soln. forming the metal. L. Liebmann reduced a beryllium mineral by electrolysis between metallic electrodes in the presence of fluorine or one of its compounds, either alone or with the addition of a halogen compound of an alkali earth. When a reducing agent, such as carbon, is added to the above mixture, and it is exposed to a white heat, or to that of the electric current, the beryllium carbide developed may, if necessary, be decomposed by suitable admixtures.

Beryllium metal has a dark steel-grey **colour,** and the crystals have a bright metallic lustre. According to P. Lebeau,[2] the **crystals** produced by electrolysis are hexagonal lamellæ, while, according to W. C. Brögger and G. Flink, the hexagonal crystals are holohedral, and are prismatic and tabular, with an axial ratio $a:c = 1:1·5802$. L. W. McKeehan obtained the **X-radiogram** of the hexagonal crystals which resembles more those of the elements magnesium, zinc, and cadmium, than those of the alkaline earth metals. Here $a = 2·283 \times 10^{-8}$ cms., and $c/a = 1·58$. W. L. Bragg gave $0·115\mu\mu$ for the radius of the at. spheres of beryllium. Beryllium is lighter than aluminium. The **specific gravity** of the crystals produced by electrolysis, according to P. Lebeau, is 1·73 at 15°; and, according to T. S. Humpidge, those produced by the sodium reduction process have a sp. gr. 1·85 at 20°. F. Fichter and K. Jablczynsky found a sp. gr. 1·842. Several of the early reports of the sp. gr. of the metal referred to impure metal—H. Debray, for example, gave 2·1; L. F. Nilson and O. Pettersson, 1·64; and J. E. Reynolds, 2·0 to 2·13. F. Fichter and K. Jablczynsky say that the regulus of metal has a **hardness** between 6 and 7 on Mohs' scale, and scratches glass at ordinary temp.;

beryllium is brittle, but at a higher temp. it is ductile, and it can be hammered, forged, rolled, and polished.

J. H. Pollok said that in an inert atm. the metal volatilizes without fusion, but L. F. Nilson and O. Pettersson claimed that the metal can be fused under press. Both statements give a wrong impression, for F. Fichter and K. Jablczynsky found that the **melting-point** of the metal is 1280° ± 20° at ordinary press.; G. Oesterheld placed the m.p. of the metal at 1278° ± 5°. H. Debray's statement that the metal melts at a lower temp. than silver is therefore wrong. W. Guertler and M. Pirani give 1300° as the best representative value. F. Fichter and E. Brunner added that the metal readily volatilizes at 1530°, under 5 mm. press. in hydrogen. G. Oesterheld made an approximate determination of the **heat of fusion** by comparing the duration of the arrest when equal volumes of gold and beryllium are cooled under similar conditions, and found 271 cals., while Crompton's rule (At. wt. × ht. of fusion ÷ absolute temp. of fusion = 2) gives a value 341. Beryllium has the largest heat of fusion of any metal, and this corresponds with its high m.p. and low at. wt. The **specific heat** of beryllium has attracted some attention, (i) on account of its value in determining the at. wt. of the element, and (ii) on account of its abnormal value at ordinary temp., as is the case with boron, carbon, and silicon. J. E. Reynolds found the sp. ht. to be 0·642 at 100°; L. F. Nilson and O. Pettersson calculated the sp. ht. of the pure metal to be between 0·3950 and 0·4005 between 0° and 46·3°; 0·4242 between 0° and 99·97°; 0·4750 between 0° and 214·0°; and 0·5055 between 0° and 299·5°. J. E. Reynolds attributed the difference between his results and those of L. F. Nilson and O. Pettersson to be due to the latter having used crystalline metal while he used amorphous. T. S. Humpidge found the sp. ht. of a specimen with 4·71 per cent. of beryllia, 1·32 per cent. of iron, and a trace of silicon to be 0·4316, from which he calculated the pure metal to have a sp. ht. of 0·4453. Another sample with 99 per cent. of beryllium, 0·43 per cent. beryllia, and 0·57 per cent. of iron, calculated for 100 per cent. beryllium, is

	0°	100°	200°	300°	400°	500°
Sp. ht.	0·3756	0·4702	0·5420	0·5910	0·6172	0·6206

The sp. ht. thus remains practically constant at 0·62, between 400° and 500°, and T. S. Humpidge represents the relation between the sp. ht. and the temp. θ, by the empirical formula $C = 0{\cdot}3756 + 0{\cdot}00106\theta - 0{\cdot}00000114\theta^2$. J. Dewar found 0·0137 for the sp. ht. of beryllium at the temp. of liquid air; and 0·125 for the at. ht. G. N. Lewis and co-workers found the atomic **entropy** at 25° and 1 atm. press. to be 31·8.

R. Thalén[3] first studied the **spectrum** of beryllium, and found it to be characterized by lines of equal intensity, one 4572·0 in the blue, and another 4488·5 in the

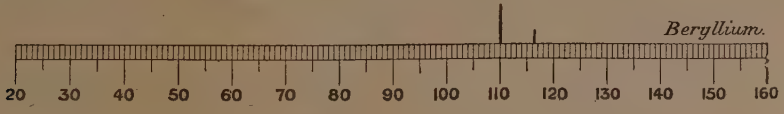

FIG. 1.—Spectral Lines of Beryllium.

indigo, although R. Bunsen said, in 1876, that neither the spark nor the flame spectrum of beryllium shows any specially characteristic lines. The spectrum of beryllium is poor in lines. W. N. Hartley studied the arc spectrum of the chloride, and found in addition to R. Thalén's two lines, 3320·5, 3130·2, 2649·4, 2493·2, and 2477·7, the second being the strongest and most persistent; he also found that the lines 3130·2 and 2477·7 are still visible in soln. of beryllium salts when the conc. has fallen as low as 0·000001 per cent. H. A. Rowland and R. R. Tatnall found the most prominent lines between 2100 and 4600 to be 2348·697, 2350·855, 2494·532, 2494·960, 2650·414, 2651·042, 3130·556, 3131·200, 3321·218, 3321·486, and 4572·869. R. A. Millikan measured the spectrum in the extreme ultra-violet. According to W. N. Hartley, beryllium oxide is reduced in the oxy-hydrogen flame by a purely chemical process: $BeO + H_2 = Be + H_2O - 97{\cdot}4$

Cals. The oxide is not fusible and not volatile under these conditions, so that the spectrum with the oxy-hydrogen flame is due to the vapour of the metal. C. M. Olmsted studied the band spectrum of beryllium chloride. L. C. Glaser found the structures of the band spectra of beryllium and aluminium are similar. J. Formanek found that when a soln. of the chloride is treated with alkanna tincture it gives a strong orange-red **fluorescence,** and gives three absorption bands. J. L. Soret found soln. of the chloride give no absorption bands, and only a feeble bluish fluorescence. W. Crookes obtained a beautiful blue **phosphorescence,** but no spectral rays, by exposing beryllia to the cathode rays in a vacuum tube. E. Rutherford and J. Chadwick obtained little, if any, evidence of the emission of long-range particles, detected by the scintillations on a zinc sulphide screen, when **α-particles** pass through beryllium. J. C. McLennan and M. L. Clark found 16·0 and 28·0 for the critical voltages for the L-series of X-rays of wave-length $\lambda=770{\cdot}7\times10^{-8}$ cms. and $428{\cdot}1\times10^{-8}$ cms. respectively.

It has been stated that beryllium is a better conductor of electricity than copper or even silver. According to F. Fichter and K. Jablczynsky,[4] the specific **electrical conductivity** is $5{\cdot}41\times10^4$ rec. ohms. When beryllium is used as anode in a soln. of sodium ammonium phosphate, it acts as a rectifier similarly to aluminium. S. Meyer found its **magnetic susceptibility** to be +0·79 at 15°. P. Pascal has found the at. coeff. of magnetization to be -113×10^{-7} units. A. Günther-Schulze studied the **electrolytic valve action** of beryllium in aq. salt soln.

Beryllium is slightly less basic than magnesium. B. Brauner[5] sums up the chemical nature of this element symbolically by stating that in their chemical properties, Si : Be=Be : B ; and Li : Na=Be : Mg=B : Al ; and Si : Mg=Be : Al =B : Si. According to H. Debray, beryllium does not combine directly with **hydrogen**, although C. Winkler thought that he had made some *beryllium hydride* by reducing beryllia with magnesium in an atm. of hydrogen. About 0·33 per cent. of hydrogen was retained by the reduced product. P. Lebeau could not prepare a hydride under these conditions. According to F. Wöhler, beryllium is not oxidized in air at ordinary temp., but when beryllium is ignited in air, it burns vividly, forming a white earth, and in oxygen, it burns very brilliantly, and the resulting oxide shows no signs of fusion ; if the metal is contaminated with the hydroxide a flame appears as the metal burns in oxygen, the flame is due to the burning of the hydrogen liberated by the decomposition of the hydroxide. A. A. B. Bussy found that beryllium oxide, BeO, is produced by the oxidation of beryllium heated in an open crucible, but the oxidation is a slow process. Beryllium is said to be as durable as aluminium on exposure to air. According to P. Lebeau, the metal is not altered by exposure to dry **air,** or to **oxygen** at ordinary temp., but if finely divided, it burns if heated *avec un vif éclat ;* the temp. of ignition varies with its state of subdivision. The finely divided metal gives brilliant sparks when projected in the flame of a bunsen burner. According to H. Debray, the compact metal does not inflame when heated in oxygen, but becomes covered with a thin protective layer of beryllium oxide, BeO, without further change ; F. Wöhler, L. F. Nilson and O. Pettersson, and J. E. Reynolds stated that beryllium is not changed by hot or cold **water.** The apparent inertness of the metal to water is due to a protective film of oxide. The truth is that it is but slowly attacked by cold water, and slowly converted into the hydroxide by boiling water. According to P. Lebeau, beryllium combines easily and directly with **fluorine, chlorine,** and **bromine,** and with rather more difficulty with **iodine ;** both F. Wöhler and H. Debray noted that combination readily occurs when the metal is heated in iodine vapour. P. Lebeau found that beryllium is violently attacked when the **hydrogen halide** gases are passed over the heated metal ; gaseous hydrogen chloride acts on the slightly warmed metal. Practically all the earlier observers—F. Wöhler, etc.—noted that beryllium is readily attacked by dil. **hydrochloric acid,** with the evolution of hydrogen. F. Wöhler stated that when beryllium is heated with **sulphur, selenium,** or **tellurium,** the sulphide, selenide, or telluride respectively is formed. F. Wöhler and others noted that the attack by dil. **sul-**

phuric acid resembles that by dil. hydrochloric acid; P. Lebeau found that with conc. sulphuric acid, the metal readily dissolves, and the acid is easily reduced to sulphur dioxide. According to F. Fichter and E. Brunner, beryllium absorbs **nitrogen** when heated above 900°, and a surface layer of beryllium nitride, Be_3N_2, is formed. The nitride is more easily formed by heating the metal in **ammonia** gas; but is not dissolved by aq. ammonia. F. Wöhler said that the metal he prepared was dissolved by cold dil. **nitric acid** with the evolution of nitric oxide; that of H. Debray dissolved with difficulty in boiling conc. acid; and that of P. Lebeau was only superficially attacked by the conc. acid. According to F. Wöhler, beryllium is attacked when fused with **phosphorus** or **arsenic,** forming respectively the phosphide or arsenide. P. Lebeau found that beryllium unites directly with **carbon** at a high temp., forming beryllium carbide, Be_2C. According to A. Cahours, beryllium replaces the iodine in **methyl iodide** and **ethyl iodide,** forming *beryllium methyl* and *beryllium ethyl;* and, according to V. Lawroff, it also replaces mercury in **mercury methyl** and **mercury propyl**, forming respectively beryllium methyl and *beryllium propyl*. P. Lebeau found that beryllium unites directly with **boron** and **silicon** in the electric arc-furnace. G. Rauter found that when the powdered metal is heated with **silicon tetrachloride** in a sealed tube for 3 hrs. at 240°–250°, a mixture of beryllium chloride and silicon is formed, together with some beryllium and undecomposed silicon tetrachloride. F. Wöhler and others noted that beryllium is attacked by an aq. soln. of **potassium hydroxide.** A number of alloys of beryllium with other **metals** have been reported—see alloys of beryllium, magnesium, zinc, and cadmium.

C. L. Parsons [6] has emphasized what he called "the vagaries of beryllium," meaning "those peculiarities of the element which stand out prominently as characteristic of itself." It has been said, probably with truth, that the literature of inorganic chemistry is overburdened with compounds which have no actual existence, but which have obtained their place and been assigned formulæ simply from the analysis of solid phases—mixed crystals, residues of evaporation, indefinite gummy precipitates, etc.—obtained under variable conditions and without other attempt to prove their individuality, and C. L. Parsons claims that the beryllium compounds are a striking illustration. The halides of beryllium—excepting perhaps the fluorides—are immediately hydrolyzed in contact with water; they are even more sensitive than the corresponding salts of aluminium. By careful manipulation of the evaporation residues, substances of almost any degree of basicity can be prepared. These are possibly all mixtures of base with the normal salt; but analyses have given rise to claims for numerous oxyfluorides and oxychlorides. Few normal salts of the non-volatile acids have been made. The sulphate, selenate, and oxalate form aq. soln., which approach soln. of the acids themselves in attacking the metals or carbonates, liberating hydrogen or carbon dioxide respectively, and reddening blue litmus. The soln. of the salts dissolve large quantities of the hydroxide, and even then the soln. attack metals and the carbonates vigorously. The normal salts of the volatile acids—carbonates, sulphites, and nitrites—cannot be made in aq. soln., but many are prepared by direct union of the oxides, or by precipitation from alcoholic soln. The normal borates, iodates, chlorates, bromates, phosphates, chromates, and acetates have not been obtained. Many basic salts have been obtained by heating conc. soln. of the hydroxide in the normal salt soln. along with beryllium carbonate. The basic precipitates are probably solid soln. of variable composition. The action of water on the compounds of beryllium is greatly modified, as is the case with magnesium, aluminium, etc., by the entrance of another element into the molecule. Hence, many double salts have been crystallized from aq. soln. in well-defined crystals under conditions where the normal salt could either not be obtained at all, or obtained only with difficulty—*e.g.* the double carbonates, chlorides, nitrates, sulphites, and iodides.

The soln. of the hydroxide in the normal sulphate, nitrate, or chloride are less hydrolyzed than the corresponding salts of aluminium and iron; while the hydroxide

can be partially removed by dialysis into water, there is little evidence of a colloidal soln. There are no signs of the formation of complex salts. This is supposed to be a case of the simple soln. of a substance (beryllium hydroxide) in a mixed solvent (water and normal salt) in one of which alone (water) it is insoluble; for the solid, when once dissolved, acts as a solvent for its own oxide or hydroxide.

Reactions of analytical interest.—The reactions of beryllium salts are in many respects like those of aluminium; they do not give precipitates in the hydrochloric acid or hydrogen sulphide groups, but, as T. J. Pelouze [7] has shown, a mixture of ammonium hydroxide and **ammonium sulphide** gives a white precipitate of beryllium hydroxide, $Be(OH)_2$, similar to that of aluminium hydroxide; hydrogen sulphide is at the same time evolved, and the precipitate is insoluble in an excess of the precipitant, but readily soluble in hydrochloric acid, forming a yellow soln. whose colour disappears on dilution. Similar results are obtained with aq. soln. of the **alkali sulphides.** A soln. of **potassium hydroxide**—or of sodium hydroxide—gives a gelatinous precipitate of beryllium hydroxide readily soluble in an excess of the reagent, but not in aq. ammonia: $Be(OH)_2+2KOH \rightleftharpoons Be(OK)_2+2H_2O$. Unlike the corresponding soln. with aluminium hydroxide, the soln. is decomposed hydrolytically on boiling, and the beryllium is re-precipitated as hydroxide provided a great excess of the alkali hydroxide be not present. This enables the two hydroxides to be separated, but to make the separation complete, the precipitate should be redissolved and reprecipitated several times. According to F. Toczyknsky, tartaric acid hinders the precipitation by alkali hydroxides; cane sugar, grape sugar, and glycerol act similarly to a smaller degree; the precipitate with baryta-water also dissolves in an excess of the precipitant, but, as L. N. Vauquelin showed, the soln. remains clear on boiling. According to C. G. Gmelin, and F. Schaffgotsch, both beryllium and aluminium hydroxides are reprecipitated from the soln. in caustic lye by the addition of **ammonium chloride.** According to C. Vincent, and C. Renz, **methylamine** or **ethylamine** precipitates beryllium hydroxide, and, unlike aluminium, but not unlike iron, the precipitate is not soluble in an excess of the precipitant. A soln. of **ammonium carbonate** produces a white precipitate of a basic beryllium carbonate, which, unlike the corresponding precipitate with aluminium, is readily soluble in an excess of the reagent. When the soln. is boiled, the basic carbonate is reprecipitated. This property enables the two compounds to be separated, but the separation is quantitative only when the carbonate is re-dissolved and reprecipitated a number of times. According to L. N. Vauquelin, and C. G. Gmelin, soln. of the **alkali carbonates** also precipitate basic beryllium carbonate, soluble only in a large excess of the sodium or potassium carbonate, and in a far smaller excess of ammonium carbonate. When the soln. of the beryllium hydroxide in alkali carbonates is boiled, a partial precipitation of beryllium as hydroxide occurs only when the soln. is much diluted. The solubility of the hydroxide and carbonate precipitates decreases with increasing age of the precipitate. If a mixed soln. of a beryllium and an aluminium salt with 10 per cent. of sodium hydrocarbonate be boiled, aluminium, but not beryllium, hydroxide is precipitated. **C. L. Parsons' test** for beryllium is as follows:

> Follow the customary procedure of qualitative analysis until the sulphides insoluble in HCl have been removed. Concentrate the filtrate so obtained to 25 cubic centimetres and when **cold** add two grams solid Na_2O_2, boil and filter. Acidify the filtrate with HNO_3 and add ammonia in excess. If no precipitate is obtained beryllium is absent. Wash any precipitate formed and add it together with two to three grams solid $NaHCO_3$ to 30 cubic centimetres (10 per cent. soln.) of water in a test-tube or casserole and bring rapidly to *boiling*. Boil for one-half minute only and filter to remove all aluminium. Dilute the filtrate with 10 volumes of water (1 per cent. soln.) and boil. Beryllium hydroxide containing a little carbonate will precipitate if present. Other elements do not interfere.

According to A. von Awdejeff, J. Weeren, H. Rose, J. M. Ordway, H. J. Debray, and F. von Kobell, when a cold soln. of a beryllium salt is digested with **barium carbonate,** beryllium hydroxide is partially precipitated in the cold, completely on

boiling. F. von Kobell stated that **calcium carbonate** does not precipitate beryllium hydroxide in the cold, but does so on boiling. Unlike thorium, zirconium, erbium, yttrium, cerium, lanthanum, or didymium salts, **oxalic acid** and **ammonium oxalate** give no precipitation with beryllium salts; but with conc. soln. of beryllium salts, potassium hydro-oxalate precipitates potassium beryllium oxalate. Unlike cerium, lanthanum, or didymium salts, **potassium sulphate** gives a fine crystalline precipitate, $Be(KSO_4)_2.2H_2O$, which is soluble in a conc. soln. of potassium sulphate. A soln. of **sodium phosphate** in presence of ammonium phosphate gives a white precipitate with beryllium salts. According to C. Rössler, an excess of a soln. of **diammonium hydrophosphate,** not disodium hydrophosphate, gives a precipitate with a beryllium salt which, when dissolved in hydrochloric acid, and the soln. just neutralized with ammonia, and boiled, gives a crystalline precipitate. The precipitation is not hindered by citric acid, while small amounts of aluminium are not precipitated; if much aluminium is present, the presence of citric acid hinders the precipitation of the beryllium ammonium phosphate. When a beryllium salt is fused with **potassium hydrofluoride,** and the cold mass extracted with water acidified with hydrofluoric acid, the beryllium fluoride dissolves, while aluminium forms a sparingly soluble potassium aluminium fluoride. According to C. A. Joy, a soln. of **sodium thiosulphate** gives a precipitate when boiled with a soln. of beryllium chloride. According to J. F. Persoz, C. A. Joy, and F. Toczyknsky, a soln. of a beryllium salt gives a precipitate when boiled with **sodium acetate;** C. G. Gmelin said the chloride is not so precipitated. L. N. Vauquelin obtained a white precipitate with **alkali succinate,** and yellow flecks with **tincture of galls.** H. Rose obtained a kind of jelly by adding **potassium ferrocyanide** to a soln. of a beryllium salt. According to J. J. Berzelius, no precipitate is given by **potassium ferricyanide, hydrofluosilicic acid,** oxalic acid, **potassium oxalate,** or **potassium tartrate.** Beryllium chloride soln. becomes dark in colour, but no precipitation occurs with **potassium thiocarbonate,** K_2CS_3. When calcined with a soln. of **cobalt nitrate,** beryllia gives a grey mass; with alumina, Thénard's blue is formed. According to A. C. Neisch, **metanitrobenzoic acid** gives no precipitate with a beryllium salt. C. L. Parsons' sodium hydrocarbonate process, and F. S. Havens' hydrogen-chloride process, previously discussed in connection with the preparation of beryllia, are recommended as quantitative processes.

Uses.—According to C. James,[8] beryllium oxide "is used in the manufacture of incandescent mantles in order to make them stronger. The amount used depends upon the manufacturer. Some makers use 5 grms. of beryllium nitrate to every kilogram of thorium nitrate, while others use only 2 grms. to the same quantity of thorium salt. Beryllium salts are useful in the manufacture of incandescent mantles. The oxide is sometimes added to material that is being used for the manufacture of abrasives." The metal has some valuable qualities, and it is said that "only the expense of production prevents the metal proving of great industrial value."

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§ 4. The Atomic Weight and Valency of Beryllium

The valency of beryllium was for many years a subject of controversy, and it incited much research. It can be argued that the element is bi- or ter-valent, although it is now generally agreed to regard it as a bivalent element. The hydrogen eq. of beryllium is nearly 4·5; if the at. wt. of beryllium is nearly 9, the element is bivalent, if 13·5, tervalent, and if 18, quadrivalent. J. J. Berzelius [1] at first regarded

beryllium as a bi- or quadri-valent element, for he formulated the oxide as either BeO or BeO_2, but in 1815, from its analogies with alumina, he considered beryllium to be tervalent, and the oxide to have a formula either BeO_3 or Be_2O_3. The specific heat law of Dulong and Petit, and the isomorphism law of Mitscherlich, seemed to favour this assumption. Thus, according to P. Hautefeuille and A. Perrey, beryllium can replace aluminium in silicates of the type $K_2O.Al_2O_3.6SiO_2$.

Beryllium occupies rather a unique position in the magnesium-zinc family group of the periodic table. It does not share with the magnesium, zinc, and cadmium salts their characteristic behaviour towards ammonia and the ammonium salts; their tendency to form double salts with other metals; the sparing solubility of their oxides in water, and their solubility in weak acids. Nor does it share the characteristics of calcium, strontium, and barium in forming soluble strongly alkaline hydroxides, sparingly soluble sulphates, soluble sulphides, and slightly soluble fluorides. In fact, beryllium is so like aluminium that until its at. wt. and the vapour density of its chloride had been determined, it was regarded as a triad element related to aluminium. A. von Awdejeff favoured the hypothesis that beryllium is bivalent, owing to the close analogy of potassium beryllium sulphate and potassium beryllium fluoride with the corresponding magnesium salts; similar remarks apply to C. Scheffer's observations on beryllium phosphate.

G. Wyrouboff further emphasized the possible tervalency of beryllium from the analogies between the beryllium silico-tungstates and the corresponding aluminium salt; J. Blake also argued in the same direction from the likeness in the physiological action of beryllium and aluminium; P. Lebeau showed that the properties of the carbides of the two elements favour the tervalency of beryllium. H. Traube's determinations of the at. soln. vol. of beryllium sulphate and chlorate are more in accord with a tervalent beryllium than with a bivalent element. Some early determinations of the sp. ht. of beryllium favoured the tervalency hypothesis, but the data were by no means unequivocal because (i) the results were discordant owing to the use of impure metal, (ii) the sp. ht. varies very much with the temp., and (iii) the elements with a low at. wt. often deviate so much from Dulong and Petit's rule that the application of the rule is not of much value as a criterion. The question was discussed by J. E. Reynolds, L. Meyer, L. F. Nilson and O. Pettersson, etc. T. S. Humpidge showed that at a high temp. when the sp. ht. becomes approximately constant, the application of Dulong and Petit's rule favours the bivalency of the element. G. Tammann showed that the vapour density determinations of aq. soln. of beryllium salts do not give a definite value for the mol. wt. H. Ley found the electrical conductivity of normal soln. of beryllium sulphate furnishes $\lambda_{32}-\lambda_{1024}=54{\cdot}2$, and has shown that although this agrees with the value for the salts of the tervalent elements, it would be wrong to assume that beryllium is tervalent because the great increase in the eq. conductivity can be explained by the hydrolysis of the salt.

The most cogent argument in favour of the bivalency of beryllium was the results of the determination of the vapour density of the chloride. The earlier observations were affected by errors through the decomposition of the salt by moist air, and not to the dissociation of the chloride. The decomposition does not occur if the salt is volatilized in a stream of hydrogen chloride or carbon dioxide. L. F. Nilson and O. Pettersson found (air unity):

	589°	597°	604°	686°	720°	745°	812°
Vap. density . . .	3·067	3·031	3·090	2·853	2·926	2·753	2·793

when the calculated value for $BeCl_2$ is 2·77. Above 1000°, the results were quite constant for $BeCl_2$. T. S. Humpidge found 2·733 and 2·714 respectively at 635° and 785°. These results are all entirely in accord with the bivalency of beryllium, and they were confirmed by observations on the vap. density of beryllium bromide by T. S. Humpidge; of beryllium acetylacetonate, $Be(C_5H_7O_2)_2$, by A. Combes; and of basic beryllium acetate, $Be_4O(CH_3COO)_2$, by G. Urbain and H. Lacombe.

S. Tanatar, however, expressed the belief that G. Urbain and H. Lacombe's compound contained two quadrivalent beryllium atoms per molecule, and not four bivalent beryllium atoms, in order to explain its constitution. This he supposes to be $R_3Be^{IV}—O—OBe^{IV}R_3$. It would, however, be legitimate to raise the question whether or not the alleged basic acetate is a chemical individual. It must also be remembered that the association of the molecules plays an important part in these determinations, for W. Biltz found the acetylacetonates of the rare earths are bimolecular in conc. soln. The mol. wt. determinations of beryllium picrate, $Be(C_6H_2O_7N_3)_2.3H_2O$, from the f.p. of its acetophenone soln., by B. Glassmann, and of that of beryllium chloride from the b.p. of its pyridine soln. by A. Rosenheim and P. Woge, are all in agreement with the bivalency of beryllium. The latter also found that the compounds of beryllium with the oxalates are quite different from those which it forms with the tervalent metals chromium, iron, or aluminium.

T. Carnelley pointed out that his determinations of the m.p. and b.p. of beryllium bromide or chloride better fitted a place in the periodic table with a bivalent than with a tervalent element; and B. Brauner made a similar observation with respect to the mol. vol. of beryllium compounds. W. N. Hartley also showed that the spectrum of beryllium corresponds with the first member of a dyad series in which calcium, strontium, and barium are homologues. L. Meyer also showed that beryllium better fits a place among the bivalent elements in the periodic table, than among the tervalent elements. D. I. Mendeléeff found that the soln. of a mol of the chloride of a metal MCl_n in 200 mols of water gives a soln. whose sp. gr. increased proportionally with the mol. wt. of the solute. If the molecule of beryllium chloride be $BeCl_2$, mol. wt. 80, it must be heavier than the molecule of potassium chloride, KCl, mol. wt. 74·5, and less than the molecule of magnesium chloride, $MgCl_2$, mol. wt. 95. On the other hand, if beryllium chloride be $BeCl_3$, mol. wt. 120, its molecule must be heavier than that of calcium chloride, mol. wt. 111, and lighter than manganese chloride, $MnCl_2$, mol. wt. 126. Experiment showed the correctness of the former assumption—at 15°/4°, the soln. $BeCl_2+200H_2O$ has a sp. gr. 1·0138; thus being greater than the sp. gr. of the soln. $KCl+200H_2O$, 1·0121, and less than that of the soln. $MgCl_2+200H_2O$, 1·0203. Hence, said he, "the bivalency of beryllium is confirmed by the dissolved and vaporized chloride."

J. J. Berzelius' determination [2] of the at. wt. of beryllium is little more than an approximation, and is of only historical interest. He determined the ratio of beryllium to chlorine in beryllium chloride, and the ratio of beryllium oxide to sulphur trioxide in beryllium sulphate, and his number, recalculated for O=16 is Be 10·6. A. von Awdejeff (1842) analyzed the sulphate, and from the ratio $BeO : BeSO_4$ computed Be=9·337; J. Weeren (1854) in the same way obtained 9·267 and G. Klatzo (1869), 9·283. H. Debray (1855) analyzed beryllium oxalate, and determined the ratio $4CO_2 : BeO$, from which he calculated the at. wt. Be=9·337. L. F. Nilson and O. Pettersson (1880) analyzed the hydrated sulphate and determined the ratio $BeSO_4.4H_2O : BeO$, from which they calculated the at. wt. Be=9·113; and G. Krüss and H. Moraht similarly obtained Be=9·062. C. L. Parsons (1904) determined the ratio $Be_4O(C_2H_3O_2)_6 : BeO$, and hence calculated the at. wt. Be =9·106 and also $Be(C_5H_7O_2)_2 : BeO$, and hence computed Be=9·103. From these results F. W. Clarke and B. Brauner have computed that the best representative value for the at. wt. of beryllium is Be=9·1, and this, too, is the value in the International Table (1920). L. Bénoist and H. Copaux infer that beryllium has an at. wt. 9·1 from a comparison of the transparency of the oxide to X-rays, with the transparencies of aluminium, sulphur, carbon, lithium, and lithium hydroxide. From the ratios $BeCl_2 : 2Ag$, and $BeCl_2 : 2AgCl$, O. Hönigschmid and L. Birckenbach computed 9·018 as the best representative value. The **atomic number** is 4. According to G. P. Thomson, the anode ray analysis of beryllium corresponds with an at. wt. $9·0 \pm 0·1$(Na=23), and no **isotopes**. No indication was found which would suggest that the atom of beryllium can lose two electrons under the conditions of the experiments.

G. Krüss and H. Moraht [3] noted the presence of a foreign substance in their ammonium carbonate soln. of beryllium hydroxide, which gave a black sulphide and a white hydroxide, implying the presence of a new element. C. L. Parsons showed that G. Krüss and H. Moraht's precipitate was probably a mixture of zinc and iron sulphides, but mainly zinc. J. H. Pollok found the precipitate contained zinc, iron, nickel, and another unknown substance. This latter he claimed to be a new element accompanying ordinary beryllium in considerable quantities because in a single fractional sublimation of the chloride in a porcelain tube, he obtained over 0·4 grm. of a chloride, which, on analysis, gave an at. wt. as high as 37; he also claimed that by a single recrystallization of the sulphate, he obtained an increase in the eq. of the metal in the first crop of crystals above the second crop. C. L. Parsons showed that J. H. Pollok's results are to be explained by the special tendency of beryllium chloride to decompose when exposed to the action of moisture, and that the access of moist air to the chloride results in a loss of chlorine. L. F. Nilson and O. Pettersson also obtained results resembling those of J. H. Pollok, and therefore took special precautions against moisture in their experiments on the vap. density of the chloride.

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§ 5. Beryllium or Glucinum Oxide

Beryllium oxide is the product of the oxidation of the metal when heated in air or oxygen. The extraction of beryllium oxide or carbonate from beryl and other minerals has already been described. The **beryllium oxide,** BeO, or *beryllia*, is prepared by calcining a salt of beryllium containing a volatile acid radicle—*e.g.* the nitrate, sulphate, oxalate, hydroxide, basic carbonate, etc.—even the chloride, bromide, or iodide yield practically all their metal as oxide when evaporated from soln., and heated; if a mixed soln. of beryllium and ammonium chlorides be so treated, a light feathery oxide is obtained which is difficult to retain in the containing vessel. J. J. Ebelmen [1] obtained it in the form of hexagonal crystals by heating beryllium silicate with an excess of potassium carbonate; and H. Debray, by strongly heating beryllium sulphate, or ammonium beryllium carbonate. P. Hautefeuille and A. Perrey obtained crystals of beryllia by fusing the oxide with beryllium

leucite; or the sulphate with silicic acid; or by fusing beryllium oxide with alkali sulphides at dull redness. The form of the crystals at high temp. is different according as potassium sulphide, sodium sulphide, or a mixture of alkali sulphide and sodium carbonate is employed. H. Grandeau heated beryllium pyrophosphate with a great excess of potassium sulphate between 1400° and 1500°, and extracted the mass with water, when there remained fine crystals of beryllia. P. Lebeau observed crystals, probably produced by sublimation, on the surface of beryllium oxide which had been melted in the electric arc-furnace.

Beryllium oxide as ordinarily prepared is a white powder. M. Levi-Malvano claimed that a blue-coloured oxide is obtained by the ignition of the hexahydrated sulphate; the colouring agent is probably some impurity, because C. L. Parsons could not verify the result. According to E. Mallard, the **crystals** belong to the hexagonal system, and have axial ratios $a:c=1:1{\cdot}6305$; they are isomorphous with those of magnesium oxide; while, according to J. J. Ebelmen, the crystals are isomorphous with alumina. W. L. Bragg estimates that the **X-radiogram** will give the zinc oxide lattice with atoms 1·78 A. apart; W. Gerlach obtained $3{\cdot}796 \pm 0{\cdot}00$ A. for the length of the edge of the elementary cube. The cubic lattice is of the sodium chloride type. It was investigated by L. W. McKeehan, who found $a=2{\cdot}696\times10^{-8}$ cms. and $c/a=1{\cdot}63$.

The **specific gravity** of beryllium oxide, unlike that of alumina, does not change sensibly by ignition, and there are no signs of polymerization. For example, P. Lebeau found at 0° for beryllia calcined at about 400°, 3·012; calcined about 1000°, 3·010; crystallized by volatilization, 3·015; and fused beryllia, 3·025. H. Rose found the sp. gr. of the powder to be 3·083 to 3·090; that precipitated and ignited in the alcohol flame, 3·090 to 3·096 at 12°; that ignited in the pottery oven, 3·201 to 3·027 (10°), and that of the crystalline oxide 3·021 (9°), so that with H. Rose the sp. gr. is less with the higher temp. of calcination. A. G. Ekeberg gave 2·967 for the sp. gr. of amorphous beryllia; G. Krüss and H. Moraht, 2·9644 (10·5°); J. J. Ebelmen, 3·02–3·06 for crystalline beryllia; L. F. Nilson and O. Pettersson, 3·016; H. Grandeau, 3·18 (14°). According to J. J. Ebelmen, the crystals of beryllia scratch quartz but not ruby, and, according to P. Lebeau, the **hardness** of the crystals from the electric arc-furnace is nearly that of corundum.

H. Davy said that beryllia neither hardens nor shrinks when heated, and fuses only at the highest temp. that can be produced. H. Caron [2] found beryllia to be infusible in the oxy-hydrogen blowpipe flame, but it volatilizes before that temp. is attained, and P. Lebeau found that the oxide can be fused and distilled in the electric arc-furnace. According to F. Fichter and E. Brunner, beryllia has a **melting-point** $2450° \pm 50°$, but is very volatile near that temp. O. Ruff, H. Seiferheld, and J. Suda gave 2525° for the m.p. of beryllia, and also found it volatilized below the m.p. E. Tiede and E. Birnbräuer said that beryllia melts at $2400° \pm 100°$, in a vacuum furnace, and that it does not volatilize much below the m.p. W. R. Mott gave 3900° for the **boiling-point** of beryllium oxide, and he added that this oxide is left as a residue by the distillation of its mixtures with the oxides of calcium, barium, strontium, magnesium, aluminium, and silicon. L. F. Nilson and O. Pettersson found the **specific heat** of the oxide to be 0·247 between 0° and 100°. According to S. Tanatar, the sp. ht. of the oxide at 100°–117° is 0·2898, and he calculated therefrom an abnormally low sp. ht. for the metal, and thence argued that beryllium is quadrivalent, exactly as the low sp. ht. of the element was previously used as an argument for the tervalency of the metal. H. Copaux and C. Philips gave for heat of oxidation $Be+O_{gas}=BeO+151{\cdot}5$ cals.; and W. Mielenz and H. von Wartenberg, $135{\cdot}9 \pm 0{\cdot}9$ Cals.

According to E. Mallard,[3] the **index of refraction** for the ordinary ray is 1·719, and for the extraordinary ray 1·733; and the double refraction is positive. H. E. Ives and co-workers studied the illuminating power and emissivity of beryllia when made into mantles and heated by Bunsen's flame. W. Crookes found that when exposed to the **cathode rays** in a vacuum tube, beryllia gives a beautiful blue **phos-**

phorescence, but no spectral rays ; it shows only a conc. of light in the blue. There is no residual glow. L. Bénoist and H. Copaux studied the **X-ray** transparency of the oxide. E. F. Nichols found that when heated to 1000° in the oxyhydrogen flame, beryllia appears blue, not red. According to L. F. Nilson and O. Pettersson, beryllia is diamagnetic ; but S. Meyer found its **magnetic susceptibility** to be zero at 16°.

According to P. Lebeau,[4] the chemical activity of beryllium oxide is dependent on the temp. at which it has been calcined. According to J. J. Berzelius, beryllia after ignition dissolves much more slowly in acids, and the affinity of beryllium oxide for the acids is less powerful than that of magnesia or yttria. The oxide is not reduced when heated in a stream of **hydrogen ;** nor is it attacked by **water.** R. Haas did not succeed in making *beryllium peroxide* by treating beryllium oxide with **hydrogen peroxide,** according to L. J. Thénard's process for zinc peroxide. The oxide was found by P. Lebeau to be attacked by **fluorine** with the formation of a fluoride. A. G. Balard stated that beryllium oxide is attacked by bromine water, especially under the influence of sunlight ; but P. Lebeau found that the oxide calcined at 440° is inert towards **chlorine, bromine,** or **iodine ;** nor do the **hydrogen halides** attack the oxide at a red heat. Conc. **hydrochloric acid** dissolves the oxide slowly, and faster if the acid be boiled, and the oxide be finely divided. A mixture of the oxide with carbon is attacked, forming the halide, when heated in a stream of a hydrogen halide. L. Meyer found the anhydrous chloride is formed when the oxide is heated in a stream of **carbon tetrachloride** vapour ; and F. Bourion found that the chloride is similarly formed when the oxide is heated to redness in a stream of **sulphur chloride** vapour. L. N. Vauquelin found that beryllium oxide is not changed when heated with **sulphur.** Conc. **sulphuric acid** readily attacks the oxide, forming the anhydrous sulphate, which, according to P. Lebeau, dissolves but slowly when the mixture is diluted with water, owing to the gradual hydration of the salt. According to P. Lebeau, beryllium oxide is reduced at a high temp. by **carbon,** forming the carbide —E. Tiede and E. Birnbräuer said the reduction begins at about 2400°. P. Lebeau also found that beryllia is reduced by **boron** forming the boride, and by **silicon** forming the silicide. The oxide is not acted on by **carbon dioxide ;** and, according to E. Frémy, the vapour of **carbon disulphide** does not convert the heated oxide into sulphide. Beryllium oxide is dissolved more slowly by conc. **nitric acid** than by conc. hydrochloric acid. H. Rose found that beryllia partially decomposes soln. of **ammonium chloride,** but the beryllia loses this property if pre-calcined ; he also found that the oxide is only partially decomposed by heating it with ammonium chloride. According to P. Lebeau, beryllia is not reduced by **potassium, sodium, magnesium,** or **aluminium**—*vide* beryllium hydride—and L. Franck found that aluminium forms an alloy when heated to a high temp. with beryllium oxide ; it is also reduced by carbon in the presence of other metals, like copper, with which the beryllium forms alloys. K. A. Hofmann and K. Höschele found that beryllium oxide fused with **magnesium chloride** furnishes volatile beryllium chloride. According to H. Debray, fused **potassium hydroxide** readily dissolves beryllium oxide, and, according to C. A. Joy, the molten mass is soluble in water. J. Weeren, and A. Atterberg stated that water does not dissolve the beryllia. C. G. Gmelin, and H. Debray also stated that beryllia is not soluble in an aq. soln. of potassium hydroxide. According to J. J. Ebelmen, beryllia is readily dissolved by fused **potassium hydrosulphate.**

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§ 6. Beryllium or Glucinum Hydroxides

According to C. L. Parsons, **beryllium hydroxide,** $Be(OH)_2$, is one of the most interesting compounds of beryllium. As previously indicated in connection with the reactions of beryllium salts, beryllium hydroxide is precipitated from soln. of beryllium salts by aq. ammonia, ammonium sulphide, alkali hydroxides, barium carbonate, methylamine or dimethylamine, and ethylamine or diethylamine. Soln. of normal carbonates precipitate a mixture of basic beryllium carbonate and the hydroxide ; the former can be almost entirely eliminated by boiling the mixture. According to J. Weeren,[1] and A. Atterberg, the normal hydroxide, $Be(OH)_2$, is precipitated by boiling a soln. of beryllium oxide in potassium hydroxide and by digesting with water the product of fusing beryllia with potassium hydroxide. C. L. Parsons, W. O. Robinson and C. T. Fuller obtained beryllium hydroxide of a high degree of purity, by dissolving impure beryllium hydroxide in a soln. of ammonium carbonate, and precipitating the basic carbonate with steam. The precipitate is washed with hot water, and boiled with water, while a stream of air was passed through the liquid. The water is frequently renewed, and the product then contains very little ammonia or carbon dioxide.

J. M. van Bemmelen distinguished two forms of the hydroxide, the one, which he called the **α-beryllium hydroxide,** is granular, and the other, the **β-beryllium hydroxide,** is gelatinous. The β-hydroxide is precipitated by ammonia from a soln. of beryllium sulphate ; it is washed with cold water out of contact with air ; dried in a stream of air freed from carbon dioxide, and powdered. Its composition approximates to $BeO.1{\cdot}61H_2O.0{\cdot}025CO_2$, and when washed and dried in air, $BeO.2{\cdot}63H_2O.0{\cdot}05CO_2$, but it has not a constant composition. The α-hydroxide is prepared by precipitation from alkaline soln. of the oxide. A soln. of the β-hydroxide in sulphuric acid is precipitated by potassium hydroxide, and redissolved by an excess of the alkali. The soln. is then diluted with water and boiled. The granular deposit is then washed with hot water, while air is excluded. It is a fine white crypto-crystalline powder, is free from carbon dioxide, and has the composition

$BeO.H_2O$. In general, J. M. van Bemmelen concludes that α-beryllium hydroxide is a chemical individual of definite composition, $Be(OH)_2$, like the hydroxides of calcium or magnesium, while β-beryllium hydroxide is of indefinite composition and behaves like the gelatinous aluminium and ferric hydroxides; it may therefore be regarded as **colloidal beryllium oxide,** for there is little to show that the water is other than adsorbed or mechanically held. This explains A. Atterberg's claim to have prepared a number of hydrated beryllium hydroxides—$Be(OH)_2.\frac{1}{3}H_2O$; and $Be(OH)_2.2\frac{1}{3}H_2O$. These may be regarded as different stages in the desiccation of colloidal, or β-beryllium hydroxide.

J. M. van Bemmelen measured the water content of the crystalline and colloidal forms of the hydroxide, $BeO+nH_2O$, dried over conc. sulphuric acid and then heated to different temp.

		15°	50°	75°	100°	125°	150°	180°	200°	212°
nH_2O	Crystalline	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	0·95
	Colloidal	1·47	1·40	1·29	1·18	1·08 (14)	1·12 (11)	1·0	1·0	—

The numbers in brackets refer to the time, in hours, the hydrate was heated. The composition of the colloidal form gradually and constantly changes owing to the loss of water with a progressively rising temp., and to the passage of the colloidal or β-form into the crystalline α-form between 150° and 180°. The composition of the crystalline or α-form remains constant with a progressively rising temp., and it begins to dissociate just over 200°; and at higher temp. he finds:

		220°	235°	250°	280°	Red heat.
nH_2O	Crystalline	0·18	0·16	0·14	0·13	0·00
	Colloidal	0·50	0·45	0·42	0·36	0·00

Crystalline, or α-beryllium hydroxide absorbs as much as $0{\cdot}25$ to $0{\cdot}5H_2O$ from air sat. with moisture, but the absorbed water is given up again in dry air; after losing $\frac{1}{2}H_2O$ near 200°, the constitution is definitely changed, for it absorbs a mol of H_2O from moist air at 15°, but gives it up again in dry air; after heating to 280°, the water of the crystalline hydroxide is reduced to $0{\cdot}13H_2O$, and it again absorbs a mol of water at 15°, but gives it up again in dry air only till the residue is reduced to $0{\cdot}18H_2O$; and after heating to redness it behaves in the same way, but a strong red heat changes it altogether, for it then loses all power of absorbing water. When the colloidal or β-hydroxide has been heated to about 215°, it undergoes changes similar to the α-hydroxide. The changes which the β-compound undergoes during heating are like those observed by M. Berthelot with ferric hydroxide, for he found that from the time when it was precipitated, it constantly changed, and at no period could be represented by a single formula. J. M. van Bemmelen attributed this behaviour of the colloidal hydroxide to its being a mixture of hydroxides which behave differently at the same temp., that is, each one requires a different temp. to convert it into the lower hydroxide or anhydride.

When a soln. of beryllium sulphate is dropped into one of potassium hydroxide, a saturation point is reached depending on the conc. of the hydroxide. The beryllium hydroxide in soln. is considered by B. Bleyer and S. W. Kaufmann to be an unstable *A*-form; the hydroxide which separates from this soln. is in the *B*-form; and when the *B*-form is dried it passes into a third *C*-form. The solubilities of these three modifications of beryllium hydroxide in soln. of potassium hydroxide of different conc., are shown in the curves, Fig. 2, and expressing conc. in mols per litre, at 18°:

	A-form.			*B*-form.			*C*-form.		
KOH	0·90	2·02	2·90	0·49	2·07	2·69	1·0	2·5	3·5
BeO	0·100	0·3273	0·5140	0·0196	0·0809	0·1071	0·0139	0·0518	0·0948

Analyses after washing show that the *A*-form is $H_2Be_2O_3$; while the *B*- and *C*-forms are H_2BeO_2. The ionic constants of the *A*-, *B*-, and *C*-forms are respectively $k_1=0{\cdot}73\times10^{-29}$; $k_2=0{\cdot}28\times10^{-29}$; and $k_3=0{\cdot}144\times10^{-29}$; and the constants of

the acid dissociation, respectively $1{\cdot}5\times10^{-12}$, $0{\cdot}56\times10^{-12}$, and $0{\cdot}29\times10^{-12}$. Freshly prepared beryllium hydroxide is a somewhat stronger acid than zinc hydroxide in the corresponding state.

J. Thomsen found the **heat of neutralization** of beryllium hydroxide to be $Be(OH)_2+H_2SO_4+Aq.=16{\cdot}1$ Cals.; $Be(OH)_2+2HCl+Aq.=13{\cdot}64$ Cals.; and E. Petersen, $Be(OH)_2+2HF+Aq.=19{\cdot}683$ Cals. J. K. Wood found that the weak beryllium hydroxide has the dissociation constant, $K=5{\cdot}2\times10^{-11}$. S. Glixelli measured the **electro-osmosis** of beryllium hydroxide. S. Meyer found the **magnetic susceptibility** of the hydroxide to be zero at 16°. P. Pascal found the mol. coeff. of magnetization to be -82×10^{-7} units.

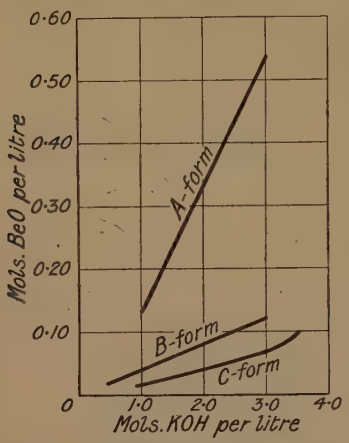

FIG. 2.—Solubilities of the Different Forms of Beryllium Hydroxide in Solutions of Potassium Hydroxide.

The properties of beryllium hydroxide vary greatly with its mode of preparation. Conc. soln. of one eq. of the normal salts can dissolve two to five eq. of the hydroxide—*e.g.* the oxalate or the sulphate dissolves nearly 3 eq., the chloride, 4 eq., and the acetate nearly 6 eq.—and the hydroxide is reprecipitated by dilution; but the precipitation is never complete by the dilution of conc. soln. The solubility of the hydroxide, and its sensitiveness to reagents, are much diminished if it has been dried by warming, or boiled for a long time in water. When beryllium hydroxide is first precipitated by alkalies it is very voluminous, and absorbs carbon dioxide, and is easily soluble in potassium hydroxide and carbonate, in ammonium carbonate, and acids. On standing it gradually passes into a more stable form, which is granular, less affected by carbon dioxide, and is insoluble in potassium carbonate, dil. alkalies, and dil. acids. It is rapidly dissolved by hot 10*N*-KOH. When beryllium hydroxide is dissolved in glacial acetic acid about 90 per cent. can be extracted by shaking it with chloroform. Iron acetate is not extracted from its aq. soln. by chloroform; so that the separation of beryllium acetate is hence an easy one.

F. Haber and G. van Oordt [2] were so impressed by the change in the sensitiveness of beryllium hydroxide with ageing, that they postulated the existence of two modifications—the freshly precipitated form readily acted on by reagents, and the second older form produced by standing or by boiling the former; the aged form is much less readily attacked and is practically insoluble in acids and alkalies. G. van Oordt said that *the ageing of beryllium hydroxide* is produced by heating it in (i) a current of steam; (ii) in an aq. soln. of an indifferent compound like sodium carbonate or ammonia; or (iii) in a very dil. soln. of alkali hydroxide, potassium carbonate, etc.

C. L. Parsons and E. J. Roberts found that the freshly precipitated hydroxide, washed by cold water, will take up one-third of an eq. of **carbon dioxide,** while the boiled hydroxide or the hydroxide which has stood for a long time is but little affected by that gas. F. Sestini stated that beryllium hydroxide is almost insoluble in water charged with carbon dioxide—100 c.c. of water sat. with that gas at ordinary temp. dissolve 0·0185 grm. BeO. P. Raikow stated that a basic carbonate is probably formed. H. Rose found beryllium hydroxide to be readily soluble in **acids;** and to be decomposed by boiling with aq. soln. of **ammonium salts;** and under these conditions, J. J. Berzelius found that beryllium hydroxide dissolved, while aluminium hydroxide remained insoluble. W. Herz found beryllium hydroxide to be virtually insoluble in soln. of ammonium salts. H. J. Debray, C. A. Joy, and C. L. Parsons studied the same reaction. Basic beryllium acetate, $Be_4O.(C_2H_3O_2)_6$, is a unique salt. The salt is prepared by dissolving the carbonate in hot glacial

acetic acid from which it separates. Beryllium also forms basic salts with formic, propionic, and butyric acids. The basic formate is difficult to purify by sublimation, (1) owing to the high temp. required, and (2) owing to its decomposition during sublimation; the basic acetate, $Be_4O(C_2H_3O_2)_6$, is readily sublimed without decomposition; it melts between 283° and 284°, and boils between 330° and 331°. It is almost insoluble in water, but is slowly hydrolyzed by cold and rapidly by hot water. It dissolves unchanged in many organic solvents—chloroform, alcohol, etc. The normal salt has not been made. Mineral acids liberate acetic acid. It is stable in dry air.

J. M. van Bemmelen found that after having been heated to redness, beryllium oxide is soluble only in boiling **sulphuric acid.** According to F. Toczyknsky, beryllium hydroxide is nearly insoluble in **hydrocyanic acid.**

According to J. Weeren, freshly precipitated beryllium hydroxide is somewhat soluble in aq. **ammonia,** but not if ammonium chloride or sulphide is present; and, according to C. Renz, beryllium hydroxide is quite insoluble in **methylamine, ethylamine, dimethylamine,** and **diethylamine.** According to L. N. Vauquelin, a conc. soln. of **ammonium carbonate** slowly dissolves beryllium hydroxide; and conc. soln. of **sodium hydrocarbonate** act similarly. C. L. Parsons and S. K. Barnes found a boiling sat. soln. of sodium hydrocarbonate readily dissolves beryllium hydroxide, but it is almost insoluble in a dil. soln.; consequently, a conc. soln. of sodium hydrocarbonate which has dissolved beryllium hydroxide when diluted so as to contain 2 per cent. or less $NaHCO_3$, slowly hydrolyzes in the cold, and deposits basic carbonate; the change occurs immediately if the soln. be boiled. Beryllium hydroxide is almost insoluble in a soln. of normal **sodium carbonate,** but, according to F. von Schaffgotsch, it dissolves in a soln. of **potassium carbonate;** and it is very slightly soluble, according to C. G. Gmelin, in a soln. of **lithium carbonate.**

According to C. G. Gmelin, beryllium hydroxide precipitated by aq. ammonia by the dilution of the soln. of beryllium hydroxide in aq. potassium carbonate, or after boiling with aq. ammonia, dissolves in a cold aq. soln. of **potassium or sodium hydroxide;** but that precipitated by boiling an alkaline soln. of beryllium hydroxide is not soluble in an aq. soln. of potassium hydroxide, ammonium carbonate, or potassium carbonate. J. Rubenbauer found the more conc. the soln. of sodium hydroxide the greater the proportion of beryllium hydroxide dissolved. Thus, at 20°, in grams per 100 c.c. of soln.:

NaOH	2·917	5·840	7·585	18·310
$Be(OH)_2$	0·850	2·094	2·789	6·760

At room temp., the solubility of freshly precipitated beryllium hydroxide in 0·39*N*-, 0·65*N*-, and 1·99*N*-sodium hydroxide was respectively 0·06, 0·144, and 0·66 mols of beryllium hydroxide per litre. The solubilities of the hydroxide after drying for a week over sulphuric acid were about one-thirtieth of these values. F. Haber and G. van Oordt found for aq. soln. of sodium hydroxide in grams per litre of sat. soln.:

	20°–23°			50°–53°			100°		
NaOH	0·5	1·0	2·0	0·5	1·0	2·0	0·5	1·0	2·0
BeO	0·060	0·170	0·570	0·080	0·230	0·900	0·080	2·290	1·020

J. K. Wood also measured the solubility of beryllium oxide in aq. soln. of sodium hydroxide. The hydrolysis of a boiling soln. of beryllium hydroxide in a lye of potassium or sodium hydroxide is not complete if an excess of base be present; indeed, the precipitation may be entirely or partially prevented by increasing the conc. of the alkali hydroxide.

H. Ley [3] concluded that beryllium hydroxide is about eleven times as basic as aluminium hydroxide, and, like other colloidal hydroxides, it has a very great tendency to occlude other substances which may be present when it is precipitated; it is almost impossible to remove these substances by washing; as the adsorbed salts are washed out, the hydroxide passes through the filter paper. According to

J. M. van Bemmelen, the power of absorbing salts from aq. soln. is possessed by the colloidal β-hydroxide, not the crystalline α-hydroxide. M. Prud'homme, however, found that colloidal beryllium hydroxide does not act as a mordant and fix colouring matters like aluminium hydroxide.

The acidic qualities of the amphoteric beryllium oxide are illustrated by its forming a series of salts, **beryllonates** or **beryllates,** with the alkali hydroxides. Beryllium hydroxide thus behaves like a weak dibasic acid with the ions $HBeO_2'$ and BeO_2''. If the alkaline soln. be allowed to stand a long time, or if it be heated to boiling, almost all the beryllium hydroxide is precipitated. This subject is discussed in connection with the zincates. W. Ostwald added :

> The question now arises why the chemical equilibrium, which has previously existed, is now disturbed, since no new substance has been added. The answer is to the effect that the beryllium hydroxide which is precipitated is a different, and indeed a more stable and less soluble form of the hydroxide than the freshly precipitated form which is soluble in alkalies. In other words, the newly prepared soln. is supersaturated with respect to the more stable form of the hydroxide, and therefore cannot continue to exist when the latter form is present. Since this form is not present in the newly prepared soln., the precipitation can commence only after the first traces of it have been formed. At the ordinary temp. this occurs slowly but quickly when heated.

The action of the alkali hydroxides on beryllium oxide and hydroxide has already been discussed. G. Krüss and H. Moraht prepared **potassium beryllate,** K_2BeO_2, or $Be(OK)_2$, by saturating a soln. of potassium hydroxide in absolute alcohol with freshly precipitated beryllium hydroxide ; filtering through asbestos in a silver funnel ; and evaporating the soln. over sulphuric acid. A crop of crystals of potassium carbonate mixed with beryllium hydroxide first separates ; the soln. is then filtered ; and, on further evaporation, a white mass is obtained, which is washed with alcohol. A similar result is obtained by working with aq. soln., but the product is more impure. The salt is very hygroscopic, readily soluble in water, sparingly soluble in cold dil. hydrochloric acid ; and very easily attacked by the carbon dioxide of the atm. Analyses always furnish rather too high a value for potassium than is needed for $Be(OK)_2$. G. Krüss and H. Moraht obtained **sodium beryllate,** $Be(ONa)_2$, in a similar manner. and it possessed properties similar to those of the potassium salt. J. K. Wood found that about 40 per cent. of an aq. soln. of sodium beryllate is hydrolyzed in $\frac{1}{10}N$-soln. at 25°. A. Hantzsch measured the electrical conductivity of soln. of the alkali beryllates, zincates, plumbates, stannates, and germanates ; and also the rate at which the soln. saponify ethyl acetate. He hence inferred that the hydroxides of zinc, beryllium, lead, tin, and germanium all act as acids, in this order of increasing strength ; zinc and beryllium hydroxides are very weak acids, and the zinc hydroxide in alkaline soln. appears to exist mostly in the colloidal form. All five hydroxides act as monobasic acids under the conditions just indicated. The order of the hydroxides just indicated is not exactly the reverse of their order if arranged according to their strength as bases.

A. S. Komarovsky [4] attempted to make *beryllium dioxide* by the action of hydrogen peroxide on hydrated beryllium oxide, but obtained a compound with hydrogen peroxide of crystallization — **beryllium hydroperoxyhydroxide,** $3BeO.4H_2O_2.8H_2O$. Basic beryllium carbonate, $BeCO_3.5BeO.8H_2O$, by a similar treatment yields a basic dioxide, **beryllium oxydioxide,** $2BeO_2.3BeO.8\frac{1}{2}H_2O$, which is moderately stable and exhibits the general characteristics of peroxides.

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§ 7. Beryllium or Glucinum Fluoride

In 1811, J. L. Gay Lussac and L. J. Thénard [1] precipitated a fluoride of beryllium by adding acid potassium fluoride to a soln. of beryllium oxide in hydrochloric acid; and in 1823 J. J. Berzelius also made a beryllium fluoride by dissolving the oxide in hydrofluoric acid, and he described the properties of the soln., and recognized that the gum-like residue obtained on evaporation has basic properties. G. Klatzo also made some observations on the fluoride in 1869. A. Cossa and D. Pecile made beryllium fluoride by heating magnesium fluoride with beryllium sulphate. The pure salt, BeF_2, however, does not appear to have been produced until P. Lebeau's *Recherches sur le glucinum et ses composés* (1898). P. Lebeau showed that all water must be absent, for the hydrolysis which occurs during the evaporation of the aq. soln. leads to the escape of hydrogen fluoride, and the soln. becomes more and more basic, for it can hold comparatively large amounts of the hydroxide in soln. By evaporating the soln. in the presence of ammonium fluoride, or in an atm. of hydrogen fluoride, the hydrolysis can be very considerably reduced. P. Lebeau made beryllium fluoride of a high degree of purity by heating the thoroughly dried double fluoride of beryllium and ammonium, $BeF_2.2NH_4F$, in a stream of dry carbon dioxide, and cooling the product in an atm. of the same gas. He also made the fluoride by the action of gaseous hydrogen fluoride on beryllium carbide.

P. Lebeau has also described the properties of the salt he prepared. Anhydrous beryllium fluoride is a transparent glass-like mass with a sp. gr. 2·01 (15°). When heated it becomes viscid, and then more and more fluid as the temp. rises; it is a mobile liquid at 800°; and at this temp. it begins to volatilize, forming a sublimate of white deliquescent crystals. According to E. Peterson the heat of the reaction $Be(OH)_2+2F_{aq.}=19{\cdot}683$ Cals.; and O. Mulert, 20·47 Cals. For the heat of formation from beryllium hydroxide and hydrofluoric acid, *vide supra*. S. Datta studied the spectrum of beryllium fluoride. The salt does not conduct electricity. The salt dissolves in all proportions in water. Owing to the hydrolysis of aq. soln. almost any degree of basicity can be obtained, and an indefinitely large number of **beryllium oxyfluorides** produced if analysis be the only evidence of chemical individuality. P. Lebeau says the product obtained by heating the residue obtained by the evaporation of a soln. of beryllium oxide in hydrofluoric acid, and ignition at 800° is a porcelain-like substance which always has a constant composition, $2BeO.5BeF_2$, and a sp. gr. 2·3. The product forms a clear soln. with water. Beryllium fluoride is only slightly soluble in absolute alcohol, but dissolves readily in 90 per cent. alcohol.

On cooling the alcoholic soln. to −23°, a white crystalline mass is obtained which melts as the temp. rises. The salt is also slightly soluble in a mixture of alcohol and ether.

The majority of the metalloids have no action on beryllium fluoride; when heated with oxygen the fluoride is partly decomposed into an oxyfluoride or more probably oxide. Sulphur vapour has no action at 75°; it is virtually insoluble in anhydrous hydrofluoric acid, and does not form a compound; with conc. sulphuric acid, it forms hydrofluoric acid and beryllium sulphate. The alkali metals and magnesium at a red heat reduce the fluoride to metallic beryllium, but the hygroscopicity and the difficulty of fusion render the process unsuited for the preparation of the metal; the action with potassium begins at 450°; with lithium and magnesium at about 650°; and aluminium may be fused with beryllium fluoride without alteration.

In 1811, J. L. Gay Lussac and L. J. Thénard, and J. J. Berzelius in 1823, prepared **potassium beryllium fluoride,** $BeF_2.2KF$, but they made no analyses. This salt was further studied by A. von Awdejeff. Rhombic bipyramidal crystals of the salt are formed by evaporating a mixture of the constituent salts. J. C. G. de Marignac gives the axial ratios $a:b:c=0{\cdot}5708:1:0{\cdot}7395$. The crystals are soluble in 50 parts of water at 20°, and in 19 parts of boiling water. The salt decrepitates when heated and fuses at a red heat. According to H. Debray, if a large excess of beryllium fluoride be present, a solid $BeF_2.KF$ is formed, but when recrystallized, crystals of $BeF_2.2KF$ are produced. These salts were also studied by W. Gibbs, and by J. C. G. de Marignac. The individuality of $KF.BeF_2$ may be questioned, but G. Klatzo doubts the existence of both salts; P. Lebeau and J. C. G. de Marignac believe both salts exist. Similar remarks apply to two **sodium beryllium fluorides,** $BeF_2.NaF$ and $BeF_2.2NaF$, prepared by J. C. G. de Marignac; and again, it is the last-named form which is the more readily obtained in crystals. Both salts crystallize in rhombohedral prisms. According to J. C. G. de Marignac, the salt $BeF_2.2NaF$ is dimorphous, furnishing both rhombic crystals with axial ratios $a:b:c=0{\cdot}8243:1:0{\cdot}3693$; and monoclinic crystals with axial ratios $a:b:c=0{\cdot}6929:1:0{\cdot}9913$, and $\beta=99°\ 20'$. J. C. G. de Marignac failed to get definite crystals of $NaF.BeF_2$, and, as in the case of the corresponding potassium compound, its individuality is open to doubt. J. C. G. de Marignac prepared crystals of **ammonium beryllium fluoride,** $BeF_2.2NH_4F$, by evaporating a soln. of the component salts; and H. von Helmont by evaporating a soln. of beryllium hydroxide and ammonium fluoride. The crystals are either colourless needles or prisms belonging to the rhombic system with axial ratios, according to J. C. G. de Marignac, $a:b:c=0{\cdot}5688:1:0{\cdot}7367$, and isomorphous with $BeF_2.2KF$. When heated the salt decrepitates, melts, and then decomposes with the evolution of ammonium fluoride. According to H. von Helmolt, the beryllium is not completely precipitated by ammonia from the aq. soln. of this salt.

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§ 8. Beryllium or Glucinum Chloride

L. N. Vauquelin[1] obtained a soln. of the chloride in 1798, but if the attempt be made to isolate the chloride by evaporating the aq. soln., hydrolysis attended by the loss of hydrogen chloride leaves a basic salt as residue. Much of the hydrolysis, but not all, can be prevented by evaporation in the presence of ammonium chloride, or in a stream of hydrogen chloride. The anhydrous chloride, however, cannot be prepared from the hydrated salt obtained from aq. soln. by heating it in dry hydrogen chloride or in dry chlorine; the water is retained too tenaciously by the salt. Anhydrous beryllium chloride, $BeCl_2$, was not prepared until H. Rose obtained the sublimed salt in 1828 by the action of a stream of chlorine gas on an intimate mixture of carbon and beryllium oxide. Whatever be the method of preparation, the materials must be thoroughly dried if the anhydrous chloride is to have a high degree of purity. F. Wöhler prepared the salt by H. Rose's process, and also by warming the metal in chlorine gas. The metal burns brilliantly, and the chloride is sublimed. Similar methods were used by A. von Awdejeff, A. A. B. Bussy, H. J. Debray, G. Klatzo, L. F. Nilson and O. Pettersson, J. H. Pollok and T. S. Humpidge. L. F. Nilson and O. Pettersson also prepared the anhydrous chloride by the action of dry hydrogen chloride on the metal. H. J. Debray passed hydrogen chloride over the heated oxide, and P. Lebeau made the chloride by the action of chlorine or hydrogen chloride on heated beryllium carbide. L. Meyer passed carbon tetrachloride over heated beryllium oxide; F. Bourion, a mixture of chlorine and sulphur chloride, S_2Cl_2. H. Rose (1848) also calcined the oxide, carbonate, or sulphate with ammonium chloride. According to K. Mieleitner and H. Steinmetz, when an ice-cold aq. soln. of beryllium chloride in ether or alcohol is sat. with hydrogen chloride, and the product is dried in vacuo, crystals of *tetrahydrated beryllium chloride*, $BeCl_2.4H_2O$, are formed; the crystals were said to contain no combined ether or alcohol. Every attempt by C. L. Parsons to make the tetrahydrated beryllium chloride, $BeCl_2.4H_2O$, prepared by A. von Awdejeff, met with failure, no crystalline chloride of any degree of hydration could be obtained, and he doubts the existence of such a compound.

Beryllium chloride is a white crystalline solid which, according to P. Lebeau, has the **melting point** 440°; T. Carnelley's 601° is much too high—J. H. Pollok's value is "about 400°." L. F. Nilson and O. Pettersson give the **boiling point** 520°, a number confirmed by J. H. Pollok. L. F. Nilson and O. Pettersson's value for the vapour density between 490° and 1520° is in agreement with the formula $BeCl_2$, and this was confirmed by T. S. Humpidge. The **molecular weight** determined by A. Rosenheim and P. Woge from the b.p. of soln. of beryllium chloride in pyridine is also in agreement with $BeCl_2$. J. H. Pollok's value for the **heat of formation** is (Be, Cl_2) 155 Cals.; W. Mielenz and H. von Wartenberg gave (Be, Cl_2)=112·6±0·4 Cals. for the heat of formation from beryllium hydroxide and hydrochloric acid, *vide supra*; the **heat of solution** of beryllium in hydrochloric acid is 199·5 Cals.; the mol. ht. of soln. in water 44·5 Cals.; and in alcohol 37·4 Cals. S. Meyer's value for the **magnetic susceptibility** is $-0{\cdot}463\times10^{-6}$ units per gram, or $-0{\cdot}038\times10^{-6}$ per mol. P. Lebeau says that the molten chloride does not conduct the electric current; W. Hampe says it does.

Beryllium chloride very readily hydrolyzes in presence of moisture—even that absorbed from the atm. The residue has this peculiarity; it readily dissolves in water in accord with the fact that one eq. of hydrochloric acid will dissolve several eq. of the carbonate. The chloride which has absorbed a trace of moisture loses chlorine, for it gives too low a value for the ratio Be : Cl, and this even when the air is dried with calcium chloride. Hence the very great care required to exclude moisture from the chloride in such determinations. Similar remarks apply to the acetate, sulphate, etc. Magnesium chloride also requires great care in drying to avoid loss of chloride resulting from the absorption of moisture from the air. When an aq. soln. of beryllium chloride is evaporated, hydrogen chloride is evolved.

J. H. Pollok found the alcoholic soln. is a conductor of electricity. According to R. Höber and F. Kiesow, the taste of soln. of beryllium chloride is due to the cation.

Beryllium chloride dissolves with great avidity in **water,** and the process is attended by a hissing sound. The soln. is hydrolyzed: $BeCl_2+2H_2O \rightleftharpoons Be(OH)_2+2HCl$, but less than the corresponding soln. of ferric or aluminium chloride. The aq. soln. have an acid reaction. The solubility of the salt and the degree of hydrolysis are both reduced by the addition of free acid. H. Ley's and L. Bruner's values for the hydrolysis of aq. soln. with 12 and 20 gram-eq. per litre are respectively 2·1 and 2·2 per cent.; and at 99·7°, with an increase from 64 to 512 gram-eq. per litre, the hydrolysis increases from 5·18 to 11·2 per cent. J. K. Wood found the **hydrolysis constant** of a *N*-soln. of beryllium chloride at 25° is 0·000232, and about 1·5 per cent. of the salt is hydrolyzed; he represents the first stage of the hydrolysis by $BeCl_2+H_2O \rightleftharpoons Be(OH)Cl+HCl$. A. Heydweiller measured the sp. gr., D, and the **electrical conductivity,** λ, of soln. with m eq. of the salt per litre; δD represents the values of $(D-1)\times 10^4$ reduced to a vacuum:

m	0·5	1·0	2·0	3·0	4·0
δD	130·9	259·5	511	761	1008
λ	58·4	51·6	42·03	34·42	29

and the residue which remains may have almost any degree of basicity according to the conditions which obtain. The evaporation of the soln. in a stream of hydrogen chloride, or mixed with ammonium chloride, and subsequent volatilization of the ammonium chloride, does not prevent the hydrolysis of the chloride. Hence, many announcements have been made of the preparation of **beryllium oxychlorides,** but these are based merely on analysis—*e.g.* A. Atterberg's claim to have made a gum-like mass of the oxychloride by the evaporation of the hydrochloric acid soln. of beryllium hydroxide; or of a soln. of beryllium chloride with the carbonate; or by precipitating a cold soln. of the chloride with ammonia. Similarly, A. von Awdejeff, A. Atterberg, and G. Krüss and H. Moraht thought they had produced **tetrahydrated beryllium oxychloride,** $BeO.BeCl_2.4H_2O$, by the slow evaporation of the chloride over sulphuric acid, but C. L. Parsons has shown that this process gives basic mixtures of varying degrees of hydration, and the product is probably a mixture of beryllium chloride and beryllium hydroxide in varying proportions. J. H. Pollok's claim to have separated beryllium chloride by fractional sublimation into a mixture of two products with different eq. was shown by C. L. Parsons to be explained by the action of water on beryllium chloride, "and that insufficient precautions were taken to guard against the presence of moisture."

According to A. Atterberg, beryllium chloride is soluble in **ether** with which it forms a crystalline compound, $BeCl_2.2(C_2H_5)_2O$; according to P. Lebeau, it behaves similarly with **alcohol,** and is but sparingly soluble in **benzene, chloroform, carbon tetrachloride,** and **carbon disulphide.** P. Lebeau also obtained compounds of beryllium chloride with **ammonia, phosphine,** and many organic bases—*e.g.* pyridine—but C. Renz was able to obtain only the quinoline compounds. According to K. Mieleitner and H. Steinmetz, the cold sublimed chloride readily unites with dry ammonia, forming **beryllium tetrammino-chloride,** $Be(NH_3)_4Cl_2$; whereas if the mixture becomes hot, **beryllium diammino-chloride,** $Be(NH_3)_2Cl_2$, is formed. F. Ephraim prepared **beryllium hexammino-chloride,** $[Be(NH_3)_6]Cl_2$, which decomposed before the dissociation press. of 500° was reached. C. L. Parsons also crystallized a compound of beryllium chloride, ether, water, and hydrogen chloride from an aq. soln. of beryllium chloride sat. with hydrogen chloride mixed with an equal vol. of ether sat. with the same gas, but K. Mieleitner and H. Steinmetz showed that the product contains no combined ether. The marked hydrolysis, the combination with, and the solubility in, organic solvents are outstanding characteristics of beryllium chloride. A. von Awdejeff, L. F. Nilson and O. Pettersson, and T. S. Humpidge state that beryllium chloride attacks **glass;** but, according to C. L. Parsons, beryllium chloride can be sublimed in hard potash glass, without the

slightest sign of action, provided all moisture is absent. The least moisture causes a thin film of oxide to form and adhere tenaciously to the glass. This film can easily be mistaken for corrosion. According to P. Lebeau, beryllium chloride does not give Friedel and Craft's reaction. **Sulphur** vapour heated with beryllium chloride forms beryllium sulphide, and sulphur chloride; **hydrogen sulphide** also converts red-hot beryllium chloride into the sulphide.

While normal beryllium chloride cannot be readily produced in the presence of water, the double-salts are much more stable, and are very much less subject to the confusing effects of hydrolysis. A. Welkow [2] failed to prepare double compounds of beryllium chloride with the chlorides of potassium or sodium; and H. L. Wells and G. F. Campbell failed to prepare the double chloride of beryllium and cæsium; in every case the single salts crystallized side by side from the mixed soln., and there were no indications of the formation of a double salt even at low temp. Beryllium thus falls in line with the series Be, Mg, Zn, Cd, Hg, in which the tendency to form double halogen salts increases with the at. wt. A. Atterberg obtained double pyramidal crystals of **auric beryllium chloride,** $AuCl_3.BeCl_2$, from a soln. of eq. quantities of the component salts; and the later crop of crystals were $BeCl_2.2AuCl_3$. R. F. Weinland and F. Schlegelmilch prepared unstable hygroscopic golden-yellow needles of **beryllium iodic chloride,** $2ICl_3.BeCl_2.8H_2O$, by passing chlorine into a hydrochloric acid soln. of beryllium chloride and iodine at 10°.

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§ 9. Beryllium or Glucinum Bromide

A. J. Balard [1] suspended beryllium hydroxide in bromine-water and found that very little passed into soln. as bromide or bromate; nor did the liquid possess bleaching qualities. F. Wöhler made the bromide by burning the metal in bromine vapour and also by the action of bromine on a heated mixture of beryllium oxide and carbon. T. S. Humpidge used a similar process, and P. Lebeau passed bromine or hydrogen bromide over heated beryllium carbide. J. B. Berthemot made a soln. of the bromide by dissolving the oxide in hydrobromic acid, and says that on evaporation crystals of beryllium bromide are formed, but A. Atterberg could not confirm this.

Anhydrous beryllium bromide sublimes in long colourless crystals, and the vapour density, according to T. S. Humpidge, is in accord with the formula $BeBr_2$. T. Carnelley and W. C. Williams gave the m.p. 600°, a number which, according to P. Lebeau, is far too high ; P. Lebeau's value is 490°, and he states that volatilization occurs below this temp. According to P. Lebeau, the fused salt does not conduct electricity ; but W. Hampe says it does, and H. N. Warren obtained the metal by the electrolysis of the fused bromide. The bromide dissolves in water with avidity, and much heat is developed. As in the case of beryllium chloride, the soln. of the bromide is much hydrolyzed : $BeBr_2+2H_2O \rightleftharpoons Be(OH)_2+2HBr$. According to J. M. Ordway, beryllium forms a basic bromide, but the remarks with reference to the oxychlorides apply also to the **beryllium oxybromides.** Beryllium bromide dissolves readily in alcohol, with which it forms a crystalline compound ; and it also combines with ammonia and organic bases.

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§ 10. Beryllium or Glucinum Iodide

F. Wöhler [1] prepared a sublimate of beryllium iodide, BeI_2, in 1828, by burning the metal in the vapour of iodine ; H. J. Debray, also, in 1875, prepared this salt by passing the vapour of iodine over the red-hot metal. We have to depend upon the work of P. Lebeau, *Sur l'iodure de glucinum*, for our knowledge of the properties of this salt ; he prepared it by leading dry hydrogen iodide or iodine vapour over beryllium carbide, Be_2C, confined in a porcelain boat, in a combustion tube at 700° ; the salt sublimes and collects in the cooler parts of the tube. It can be preserved in an atm. of dry carbon dioxide. According to P. Lebeau, sublimed beryllium iodide forms colourless needle-like crystals, which are quickly decomposed in moist air. The sp. gr. of the salt at 15° is nearly 4·2. The crystals melt at 510°, and begin to sublime below this temp. ; according to H. J. Debray, the iodide is less volatile than the chloride. The iodide boils between 585° and 595°. The slightest trace of water attacks beryllium iodide immediately, but it is not so sensitive after fusion, probably because less surface is exposed. J. M. Ordway claims to have made **beryllium oxyiodide,** but there is no satisfactory evidence of the individuality of such a compound. Beryllium iodide is insoluble in benzene, toluene, and turpentine, and very sparingly soluble in carbon disulphide. Beryllium iodide is soluble in alcohol with which it forms a crystalline compound ; likewise also with ether. Unlike aluminium iodide, it does not react upon cold carbon tetrachloride ; nor does it react with carbon hexachloride, C_2Cl_6. It reacts energetically with acetic anhydride, anhydrous chloral, and a large number of organic compounds. Ammonium compounds and organic bases—*e.g.* aniline and pyridine—form crystalline compounds with beryllium iodide.

When beryllium iodide is heated in oxygen it takes fire near a red heat, forming, according to H. J. Debray, beryllium oxide and iodine. Beryllium iodide vapour burns in air, it can be distilled unchanged in dry hydrogen, nitrogen, or carbon dioxide ; but chlorine or bromine readily displace the iodine, and fluorine both displaces the iodine and unites with it, forming iodine fluoride—the attack by chlorine

and fluorine proceeds in the cold with the evolution of light and heat. Sulphur acts on heated beryllium iodide, forming beryllium sulphide; hydrogen sulphide forms white sulphide; and phosphorus, beryllium phosphide; at a red heat, cyanogen reacts with beryllium iodide, forming a white solid, which is less volatile than the iodide, and which with water gives a soln. reacting like a cyanide and is probably *beryllium cyanide*, $BeCy_2$. Beryllium iodide in the cold absorbs large amounts of ammonia, forming white pulverulent **beryllium sesquiammino-iodide,** $2BeI_2.3NH_3$, which melts readily and crystallizes on cooling. If heated in ammonia gas, a higher ammino-compound appears to be formed. Sodium, potassium, and lithium reduce beryllium iodide at about 350°; magnesium, at about 450°; and aluminium, silver, copper, and mercury do not react below the temp. of the softening of glass.

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§ 11. Beryllium or Glucinum Sulphide and Sulphates

L. N. Vauquelin [1] found that beryllium oxide is not changed when heated with sulphur. F. Wöhler believed that he had made **beryllium sulphide** by heating the metal with molten sulphur, but both H. Debray, and L. F. Nilson and O. Pettersson failed to get evidence of a combination of the two elements, nor could E. Frémy produce the sulphide by passing the vapour of carbon disulphide over heated beryllium oxide. J. J. Berzelius claimed to have made a double sulphide of beryllium and tungsten, but this has not been confirmed. P. Lebeau, however, made beryllium sulphide by heating the anhydrous chloride or iodide with sulphur or with hydrogen sulphide; and by the action of sulphur vapour on the carbide at a high temp. K. Mieleitner and H. Steinmetz prepared it by heating beryllium chloride in hydrogen sulphide purified by means of a chromous salt and phosphoric acid. Beryllium sulphide is a white pulverulent solid, which P. Lebeau said is immediately decomposed by water, but which, according to K. Mieleitner and H. Steinmetz, is little decomposed by water even when boiling; but is readily attacked by acids including atm. carbon dioxide. It burns with a bright flame; in contact with conc. nitric acid, sulphur is separated; dry hydrogen chloride, at a red heat, converts it into the chloride; and dry bromine, at a red heat, converts it into the bromide. A *beryllium polysulphide* has not been prepared.

In 1798, L. N. Vauquelin [2] prepared a gummy mass of basic sulphate by the action of sulphuric acid on beryllia. J. J. Berzelius, and H. R. Gmelin studied the beryllium sulphates in 1815, and prepared a compound which was regarded as a hydro- or acid sulphate, but which A. von Awdejeff proved to be **tetrahydrated beryllium sulphate,** $BeSO_4.4H_2O$, and he employed this salt to determine the at. wt. of beryllium. Several others—J. Weeren, G. Klatzo, L. F. Nilson and O. Pettersson, and G. Krüss and H. Moraht—employed the salt for the same purpose, but C. L. Parsons showed that when confined over phosphoric oxide, the salt lost water continuously and is not suited for determining the at. wt. of the element. Anhydrous **beryllium sulphate,** $BeSO_4$, and five hydrates—$BeSO_4.H_2O$, $2H_2O$, $4H_2O$, $6H_2O$, and $7H_2O$—have been reported, but the evidence for the heptahydrate is probably not well founded. L. F. Nilson and O. Pettersson prepared a product, which they regarded as the anhydrous sulphate, by heating the hydrate to 250°; and M. Levi-Malvano obtained it by gradually heating the hydrate to 180°, and he claims to have completely eliminated all the water between 218° and 220°. According to C. L. Parsons, however, the water of crystallization is not all expelled even at 250°; and there is no sharply defined line between the points where all the water is driven

off, and where sulphuric anhydride begins to be evolved, in fact, they come off together over a considerable range of temp. A product which is almost anhydrous and which has lost no sulphuric anhydride can be obtained at a temp. near the b.p. of sulphur. P. Lebeau prepared an anhydrous sulphate by the action of conc. sulphuric acid on beryllium oxide, and evaporating off the excess of acid. Here again C. L. Parsons claims that it is next to impossible to evaporate the last traces of free acid and water resulting from its decomposition, without decomposing a small amount of the sulphate, and furnishing a product which leaves a small proportion of residue after the main portion has dissolved.

Tetrahydrated beryllium sulphate was prepared by J. J. Berzelius by dissolving the oxide, hydroxide, or carbonate in an excess of sulphuric acid, and removing the excess of acid by evaporation. The crystals were washed with alcohol. A. von Awdejeff recrystallized Berzelius' product from hot water.

C. L. Parsons proceeds by evaporating the sulphuric acid soln. of beryllia in a platinum dish, and heating it below a red heat until the larger part but not all the white fumes of sulphuric acid have been driven off. The product is dissolved in water, evaporated to the point of crystallization. A very slight excess of beryllia in the soln. prevents the formation of the crystals, and yields a non-crystallizable syrup. The crystals can then be purified by washing with conc. alcohol, re-solution in water, evaporation to a syrup and pouring, while hot, into excess of conc. alcohol. The soln. is at first colloidal, but after some hours the $BeSO_4.4H_2O$ crystallizes out almost completely. By repetition, the last traces of sulphuric acid may be removed; or, more quickly, beryllium oxide may be dissolved in conc. sulphuric acid in a platinum dish and the excess of sulphuric acid be driven off by a Bunsen burner, held in the hand. Care must be used to heat but little higher than necessary to remove the excess of acid. The mixture of anhydrous sulphate with a little oxide, resulting from its own decomposition, is then treated with water and allowed to stand. While quite insoluble at first, the sulphate will have dissolved in the course of one or two days. Filtration from the undissolved oxide and crystallization yields a product of a fair degree of purity.

A. Atterberg prepared **dihydrated beryllium sulphate,** $BeSO_4.2H_2O$, by drying the tetrahydrate at 100°. It was also prepared by L. F. Nilson and O. Pettersson, and G. Krüss and H. Moraht. C. L. Parsons showed that the dihydrate is fairly stable in dry air at ordinary temp., but between 100° and 110°, it slowly loses water, and, with sufficient time, the loss is continuous. The transition temp. for the tetrahydrate and the dihydrate is 113·6°, as illustrated in Fig. 3. If alcohol be added to the soln. at a temp. below 100°, or if the soln. be evaporated below this temp., the tetrahydrate is formed, and if above 100°, the dihydrate appears. M. Levi-Malvano claimed that in a sealed tube at 158°, the dihydrate passes into **monohydrated beryllium sulphate,** $BeSO_4.H_2O$. Progressive dehydration, by heating, of the tetrahydrate of beryllium sulphate confirms the existence of the di- and monohydrates, the former being obtained at 55°–60° and the latter at 100°, indicating the existence of a hemihydrate obtainable at 150–160°. The anhydrous salt obtained at 250° is stable up to 530°–540°, and thus allows of the estimation of beryllium in the form of its sulphate.

G. Klatzo claimed to have prepared monoclinic prisms of *heptahydrated beryllium sulphate,* $BeSO_4.7H_2O$, from a strongly acid soln., but C. L. Parsons showed that the conditions which G. Klatzo described for the preparation of the heptahydrate do not furnish any such salt. The analogies between beryllium and magnesium salts probably misled G. Klatzo into believing that possibly an imperfectly dried sulphate was analogous in composition with heptahydrated magnesium sulphate. J. C. G. de Marignac once obtained a mass of efflorescent prismatic crystals, of what he regarded as **hexahydrated beryllium sulphate,** $BeSO_4.6H_2O$, by evaporating a supersaturated soln. of sodium and beryllium sulphates. M. Levi-Malvano could not obtain crystals of the hexahydrate from soln. of the tetrahydrate; but he obtained them by the action of an excess of slightly diluted sulphuric acid on enough beryllium hydroxide or carbonate, at ordinary temp., to ensure a state of supersaturation of the sulphate. By suddenly shaking the mass, crystallization occurred. The soln. should contain an excess of acid, and inoculation with crystals of the hexahydrate

does not appear of any assistance. Crystallization in the cold did not specially favour the formation of the hexahydrate; but supersaturation seemed to be the one necessary condition. C. L. Parsons and C. T. Fuller made many attempts to produce the hexahydrate, but without success, and they attributed their failure to the omission of some essential condition other than supersaturation. Once the hexahydrate had been produced, M. Levi-Malvano found that it crystallized from aq. soln. at temp. as high as 50°, and he even threw it out of soln. at 90° by the addition of boiling alcohol; at −30°, the cryohydrate, a mixture of ice and the hexahydrate, was formed. F. Wirth also said that the solid phase in contact with sulphuric acid up to 13*N*-soln. is the hexahydrate, but H. T. S. Britton could obtain no evidence of the existence of the hexahydrate; he repeated F. Wirth's observations, and generally concluded that "if the hexahydrate does exist, the conditions for its preparation have not yet been described."

According to C. L. Parsons, anhydrous beryllium sulphate is almost insoluble in *water*, but it is slowly converted by cold water, and rapidly by hot water, into the tetrahydrate. The solubility of beryllium sulphate has been determined by M. Levi-Malvano. He found for the stable system:

	30·0°	40·0°	68·0°	85·0°	95·4°	107·2°	111·0°	113·6°	119·0°
Per cent. $BeSO_4$	30·5	31·9	38·3	43·3	47·5	53·6	56·2	—	59·9
Solid phases	$BeSO_4.4H_2O$							$BeSO_4.2H_2O$	

where 113·6° is the transition temp. from the tetrahydrate to the dihydrate. For the metastable system, he found:

	31·0°	50·0°	72·2°	77·4°	80·0°	91·4°	105·0°
Per cent. $BeSO_4$	34·4	37·8	42·9	45·0	45·9	49·5	54·2
Solid phases	$BeSO_4.6H_2O$				$BeSO_4.2H_2O$		

The results are plotted in Fig. 3. There is a transition temp. at 77·4° for the metastable hexahydrate and the metastable dihydrate. As indicated above, the dihydrate passes into the monohydrate at 158°. Beryllium sulphate thus appears to be soluble in its own weight of water, but, as F. Ephraim has emphasized, the numbers are affected by an error due to the fact that the tetrahydrate was obtained from soln. with an excess of sulphuric acid, and F. Wirth obtained lower values for the solubilities. For example, M. Levi-Malvano obtained a solubility of one mol of $BeSO_4$ per 11·18 mols of water at 31° and one mol of $BeSO_4$ per 11·5 mol of water at 25°; or, 100 grms. of soln. contain 33·67 grms. of $BeSO_4$, or 100 grms. of water dissolve 50·78 grms. of $BeSO_4$. F. Wirth found 8·262 grms., or 0·07857 mols of $BeSO_4$, in 100 grms. of soln. The addition of small proportions of *sulphuric acid* lowers the solubility of beryllium sulphate but slightly; and with proportions beyond 12·5*N*-acid, the hexahydrate passes into the tetrahydrate, and the solubility decreases much further. The solubility in 20*N*-acid is about one-fourth of the value for water. F. Wirth gives for sulphuric acid of different normality, the following solubilities at 25° in grams per 100 grms. of soln.:

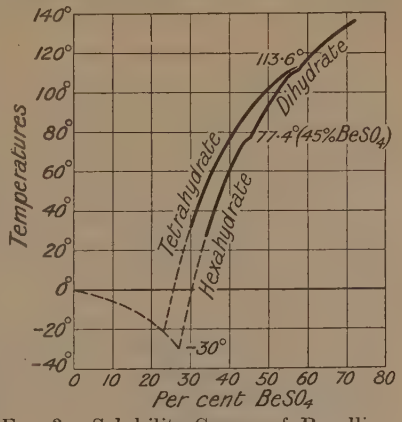

Fig. 3.—Solubility Curves of Beryllium Sulphate.

H_2SO_4	0	1·1	2·11	4·32	10·8	12·6	14·5	16·96	20·78	24·92
$BeSO_4$	8·212	8·429	7·944	6·603	5·773	6·628	5·438	3·640	2·128	2·185

The results are plotted in Fig. 4. H. T. S. Britton's results at 25° are quite different. He found the solid phase in all cases to be the tetrahydrate, and expressing the normality of the sulphuric acid by N, and the conc. of the soln. in grms. $BeSO_4$ per 100 grms. of sat. soln., he found:

N	0	3·39	5·01	8·66	13·23	16·70	19·23	20·70
$BeSO_4$	29·94	20·51	15·91	8·61	3·54	2·04	0·98	0·86

According to F. Taboury, dihydrated beryllium sulphate crystallizes from a conc. soln. of sulphuric acid, and the tetrahydrate crystallizes from a dil. soln. Magnesium sulphate crystallizes from a soln. containing much magnesium chloride and then retains four in place of seven mols of water. There is no evidence of the formation of an acid or hydro-sulphate. Tetrahydrated beryllium sulphate is insoluble in absolute *alcohol;* but, according to J. Thomsen, and H. Debray, aq. alcohol dissolves marked quantities of the salt.

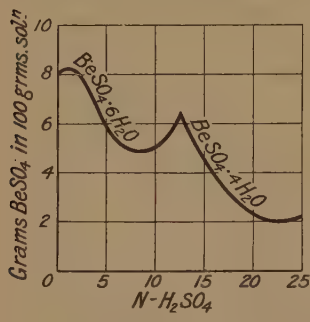

Fig. 4.—Solubility of Beryllium Sulphate in Sulphuric Acid at 25°.

According to A. von Awdejeff, the bipyramidal crystals of tetrahydrated beryllium sulphate belong to the tetragonal system, and, according to H. Töpsöe, the axial ratios are $a:c=1:0{\cdot}9461$. Observations have been made by A. E. Nordenskjöld, and G. Wulff on the multiple twinning of the crystals. According to G. Klatzo, the crystals of the unconfirmed heptahydrate are monoclinic prisms. Mixed crystals of beryllium and aluminium sulphates were studied by G. Brügelmann; J. C. G. de Marignac, A. Atterberg, and J. W. Retgers observed no signs of the formation of mixed crystals with the sulphates of copper, magnesium, zinc, manganese, iron, or nickel. According to F. Zambonini, the hexahydrate furnishes cubic crystals. L. F. Nilson and O. Pettersson gave 2·443 for the **specific gravity** of anhydrous beryllium sulphate. For tetrahydrated beryllium sulphate, H. Töpsöe gave 1·725; L. F. Nilson and O. Pettersson, 1·713; G. Krüss and H. Moraht, 1·7125 at 10·5°; and H. Stallo, 1·6743 at 22°. H. Jahn, and H. Traube measured the **molecular solution volume** of beryllium sulphate soln. with 11·283 and 20·281 per cent. soln. of beryllium sulphate and found the respective sp. gr. to be 1·09366 and 1·17874, and the mol. soln. vol. to be 23·9 and 25·7 at 14°. Beryllium has a greater soln. vol. than is usually the case with bivalent elements. J. Wagner found the **viscosity** of N-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{16}N$-soln. of beryllium sulphate, at 25°, to be respectively 1·3600, 1·1620, 1·0749, and 1·0151, when the viscosity of water is unity.

According to C. L. Parsons, the anhydrous sulphate is stable in dry air; so also is the dihydrate. According to L. F. Nilson and O. Pettersson, the crystals of the tetrahydrate are stable in dry air, but J. Weeren found that they effloresce in dry air at ordinary temp., and also, according to H. Debray, in warm dry air. C. L. Parsons found the **vapour pressure** of the tetrahydrate at 20° is equal to the press. of 20 mm. of olive oil, and increases rapidly on a rising temp.; the tetrahydrate gradually loses water of crystallization when confined over phosphorus pentoxide, and J. Weeren found the crystals lose one-third their water of crystallization at 35°. According to A. Atterberg, the tetrahydrate loses the eq. of two mols of water at 100°; at 150°, another mol of water is lost; and all is given off at 180°. L. F. Nilson and O. Pettersson found that the tetrahydrate loses two mols of water between 100° and 110°, and the rest at 250°. G. Krüss and H. Moraht also stated that all the combined water is lost at 250°. According to A. von Awdejeff, and H. Debray, the tetrahydrate first loses water, and when heated more strongly, it loses sulphur trioxide, as sulphur dioxide and oxygen, and beryllium oxide remains. J. Weeren found that no sulphur trioxide is lost at 200°. G. Marchal found the thermal decomposition between 590° and 830° corresponds with $BeSO_4=BeO+SO_3$,

and $2SO_3 \rightleftharpoons 2SO_2+O_2$; and $\log p = -14907T^{-1} - 14{\cdot}1 \log T + 57{\cdot}97$, where p denotes the partial press. of sulphur trioxide. The computed **heat of dissociation** is −53·5 cals.

According to C. L. Parsons, also, when anhydrous beryllium sulphate is heated, it begins to lose sulphur trioxide at about 400°, and as J. J. Berzelius found the decomposition is complete at a white heat. The **melting point** of the dihydrate in a sealed tube is 145°, and the molten salt boils at 150°. M. Levi-Malvano found the tetrahydrate partially melts in its water of crystallization if rapidly heated to 110°, and begins to bubble and boil. At 125°, the mass again becomes dry. The hexahydrate was found by M. Levi-Malvano to melt at 78·8°, with the separation of a mass of crystals which later pass into soln.; on cooling, the liquid freezes at 67°, and the temp. then rises to 68·4°. According to L. F. Nilson and O. Pettersson, the **specific heat** of anhydrous beryllium sulphate is 0·1978. J. Thomsen found the **heat of solution** of a mol of the tetrahydrate in 400 mols of water to be 1·10 Cals.; J. H. Pollok found 0·85 Cal. For the **heat of formation** from beryllium hydroxide and sulphuric acid, *vide supra*.

According to H. Töpsöe and C. Christiansen, the tetragonal crystals of tetrahydrated beryllium sulphate are uniaxial, optically negative, and doubly refracting. The **indices of refraction**, μ, of the tetrahydrate, averaged from measurements by G. Wulff, and H. Töpsöe and C. Christiansen, are:

	Ordinary ray.			Extraordinary ray.		
	C	D	F	C	D	F lines
μ . . .	1·4688	1·4717	1·4774	1·4336	1·4358	1·4408

J. H. Gladstone and W. Hibbert give 47·41 for the **molecular refraction** of the solid sulphate, and 47·94 for the same salt in aq. soln. H. Jahn found the **specific rotation** to be 0·28895, and the mol. electromagnetic rotation of the plane of polarization in soln. to be 1·83 (water unity). H. Ley found the eq. **electrical conductivity**, λ, of soln. with a mol of beryllium sulphate in v litres of water, at 25°, to be

v . . .	32	64	128	256	512	1024
λ . . .	66·4	77·0	88·7	99·4	112·6	124·4

Both H. Ley, and L. Bruner found that beryllium sulphate is hydrolyzed in soln., but the percentage **hydrolysis** is less than with soln. of aluminium and ferric sulphates; the latter estimates that at 40°, $\frac{1}{4}N$-, $\frac{1}{12}N$-, and $\frac{1}{20}N$-soln. are hydrolyzed respectively 0·52, 0·58, and 0·68 per cent. The aq. soln. of beryllium sulphate is strongly acid to indicators; it attacks zinc with the evolution of hydrogen; liberates carbon dioxide from carbonates; and dissolves a relatively large proportion of beryllium hydroxide or carbonate—evolving carbon dioxide in the latter instance, all of which indicate a high conc. of the hydrogen ions or free acid, although C. L. Parsons has shown that a very small excess of base completely inhibits the power to invert cane sugar. The taste of the salt appears to be both acid and sweet. R. Höber and F. Kiesow found that the sulphate and chloride have the same sweet taste at equal ionic conc. According to S. Meyer, the **magnetic susceptibility** at 18° of anhydrous beryllium sulphate is $-0{\cdot}326\times10^{-6}$ units; and of the tetrahydrate at 17° $-0{\cdot}314\times10^{-6}$ units per grm. or $-0{\cdot}071\times10^{-6}$ units per mol. A. Cossa and D. Pecile found beryllium sulphate reacts with magnesium fluoride, forming beryllium fluoride.

The basic sulphates of beryllium.—J. J. Berzelius[3] showed that a soln. of beryllium sulphate can dissolve its own hydroxide, and, guided by the law of definite proportions, he assigned formulæ, $3BeO.SO_3.4H_2O$ and $2BeO.SO_3.3H_2O$, to the evaporated gummy residues of the corresponding soln. merely because they represented whole eq. although he must have obtained residues with intermediate proportions; he also assigned the formula $9BeO.SO_3.14H_2O$ to the basic precipitate obtained by diluting the conc. soln. of $BeSO_4+2Be(OH)_2$. In 1854, H. Debray employed the basic sulphates as a method of separating beryllium from aluminium,

but he assigned no formulæ to the basic sulphates. By diluting a conc. soln. of beryllium sulphate, sat. with beryllium hydroxide, A. Atterberg also obtained a precipitate to which he assigned formulæ, $BeSO_4.5Be(OH)_2.2H_2O$ and $BeSO_4.7Be(OH)_2.H_2O$. He also evaporated soln. containing two and three eq. of the oxide to one of acid, and obtained *residua* corresponding with the formulæ given by J. J. Berzelius.

C. L. Parsons showed that the quantities of hydroxide or carbonate dissolved are proportional to the conc. of the soln. of the beryllium salt, but the proportionality is not so apparent with dil. soln. A variation in the acid radicle determines the solubility thus—the sulphate can dissolve three eq. of beryllium oxide to one of sulphate, the chloride can dissolve four eq., and, as J. M. Ordway showed, the acetate can dissolve six eq. The dilution of these soln. with water furnishes non-crystallizable highly basic precipitates; the evaporation of the soln. leaves a gummy residue. The dried precipitates and evaporation *residua* are non-crystalline and glassy, they vary in composition with the conc. of the soln. from which they are derived, and the extent to which the acid dissolved the base. By diluting the more basic soln. of beryllium sulphate C. L. Parsons indeed obtained precipitates with $BeO : SO_3$ as 25 : 1. When the precipitates are washed they become more and more basic, and finally approach the composition of the hydroxide, although the last trace of acid cannot be removed by washing. The evaporation of the mother liquid remaining after the separation of a precipitate also furnishes non-crystalline and glassy masses which are physically indistinguishable from the basic precipitates except that they are soluble in water.

C. L. Parsons, W. O. Robinson, and C. T. Fuller found that the f.p. of soln. of beryllium sulphate is raised by beryllium hydroxide, and they concluded that there is a compound formed between the normal sulphate and hydroxide giving a smaller number of effective osmotic parts; or there is an aggregation of the dissolved molecules; or the hydroxide is colloidal in its nature and interferes with the free movement of the crystalloid particles. Attempts to precipitate a soluble basic sulphate by the addition of electrolytes gave negative results. When the soln. are dialyzed, the membrane has a tendency to separate the excess of base from the normal salt, but no such separation occurs when the normal sulphate is dialyzed. The electrolysis of the soln. and measurements of the transport of the ions show that no complex anion containing beryllium is formed. The dissolution of hydroxide by soln. of the normal sulphate lowers the electrical conductivity.

It is therefore inferred that when beryllium hydroxide dissolves in a soln. of one of its normal salts, there is no evidence of the formation of a molecular complex, or of a colloidal soln. C. L. Parsons stated that the soln. of the beryllium salt acts as a solvent for beryllium hydroxide in a manner exactly analogous with the dissolution of camphor by acetic acid. It is also concluded that the so-called basic beryllium sulphates do not exist as separate and definite chemical compounds, but are in reality solid soln. of the hydroxide and sulphate, which are much more basic in composition when equilibrium with the mother liquors is reached than when first precipitated. The truly basic compounds of beryllium so far obtained, which are crystalline and of a definite composition, belong solely to the fatty acid series.

A number of hydrated double sulphates of beryllium has been prepared, but they have not all been tested by phase-rule criteria. L. N. Vauquelin[4] probably made a dihydrated **potassium beryllium sulphate,** $BeSO_4.K_2SO_4.2H_2O$, and the salt was described by A. von Awdejeff, and subsequently by H. Debray, J. C. G. de Marignac, etc. It is made by the evaporation of a soln. of eq. proportions of the component salts. The crystals are colourless and so ill-defined that J. C. G. de Marignac was unable to determine their form. A. von Awdejeff found that they are much more soluble in hot than in cold water, and, according to A. Atterberg, they lose all their water of crystallization at 100°. G. Klatzo claimed that the crystals which separated at —2° or —3° are trihydrated, $K_2SO_4.BeSO_4.3H_2O$. W. Grahmann found that potassium and beryllium sulphates form a single compound in tetragonal

crystals, potassium beryllium trisulphate, $K_2SO_4.2BeSO_4$, with a maximum on the f.p. curve at about 910°—Fig. 5. Solid soln. are not formed. H. T. S. Britton and A. J. Allmand studied the ternary system K_2SO_4—$BeSO_4$—H_2O at 25°, and obtained the results summarized in Fig. 6, the only complex observed was L. N. Vauquelin's

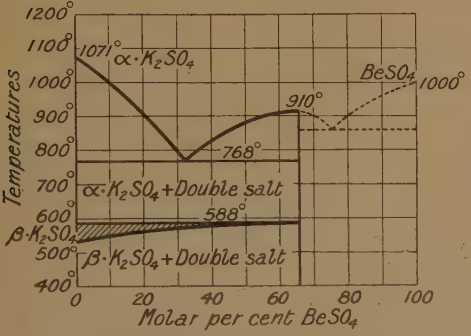

Fig. 5.—Freezing-point Curves of Binary Mixtures of K_2SO_4—$BeSO_4$.

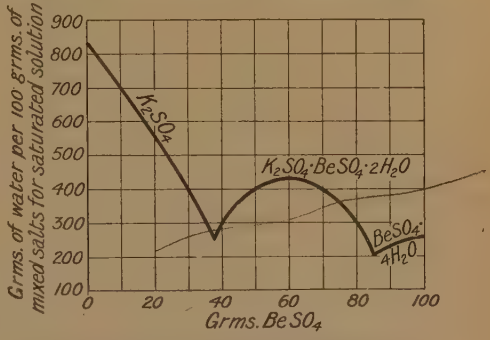

Fig. 6.—Solubility Curves of Mixtures of K_2SO_4—$BeSO_4$ in Water at 25°.

salt, $K_2SO_4BeSO_4.2H_2O$. H. Debray precipitated tetrahydrated **potassium beryllium hydrosulphate,** $2K_2O.BeO.4SO_3.5H_2O$, or $BeSO_4.K_2SO_4.2KHSO_4.4H_2O$, by adding dil. sulphuric acid to a mixed soln. of the component salts; and A. Atterberg evaporated a strongly acid soln. of eq. proportions of the component salts. The fine acicular prisms lose 11·75 per cent. (3 mols) water at 100°, and 3·31 per cent. (one mol) more at 300°; at a dull red heat, one-fourth of the sulphur trioxide is lost. A. Atterberg prepared radiating star-shaped groups of fine acicular crystals of dodecahydrated **sodium beryllium sulphate,** $2Na_2SO_4.3BeSO_4.12H_2O$, by evaporating to a thick syrup, a soln. of at least three mols of beryllium sulphate to one mol of sodium sulphate. The crystals are stable in air. A. Atterberg also prepared crystals of dihydrated **ammonium beryllium sulphate,** $BeSO_4.(NH_4)_2SO_4.2H_2O$, from the syrupy liquid obtained by evaporating a soln. of the component salts on a water-bath, and then over conc. sulphuric acid. The crystals lost all their water at 100°. H. T. S. Britton's study of the ternary system: $BeSO_4$—$(NH_4)_2SO_4$—H_2O at 25°, Fig. 7, showed that this is the only double salt stable under these conditions. G. Klatzo claimed to have made tetragonal crystals of **beryllium cupric sulphate,** $Be_4Cu(SO_4)_5.20H_2O$, isomorphous with tetrahydrated beryllium sulphate by adding an excess of beryllium sulphate to an acid soln. of the cupric salt; and triclinic crystals of $BeCu_9(SO_4)_{10}.50H_2O$, by keeping the cupric salt in excess; but, according to J. C. G. de Marignac, beryllium cupric sulphate cannot be obtained, and J. W. Retgers found that the component salts do not form isomorphous mixtures.

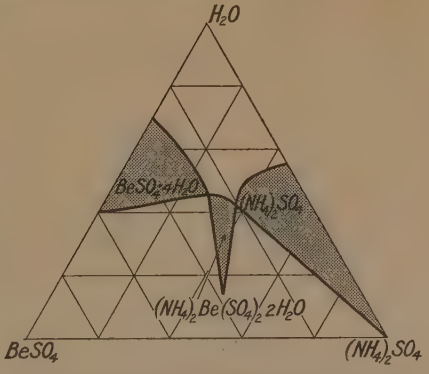

Fig. 7.—Equilibrium Phases in the Ternary System, $BeSO_4-(NH_4)_2SO_4-H_2O$ at 25°.

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§ 12. Beryllium or Glucinum Carbonate

L. N. Vauquelin noticed that beryllium hydroxide readily attracts carbon dioxide from the air; and he noted the solubility, in soln. of alkali or ammonium carbonate, of the precipitate obtained by adding an aq. soln. of ammonium carbonate to a soln. of beryllium hydroxide; and J. J. Berzelius noted the solubility of the precipitate in soln. of other ammonium salts. Normal **beryllium carbonate,** $BeCO_3$, is not known. G. Klatzo [1] claimed to have made small crystalline masses of the tetrahydrate, $BeCO_3.4H_2O$, by passing carbon dioxide into water with beryllium hydroxide in suspension, filtering, and evaporating in an atm. of carbon dioxide. He further stated that the product loses its water and one-sixth of its carbon dioxide at 100°, and half the carbon dioxide at 200°. There is, however, some mistake because the carbonate is so readily hydrolyzed by water that in aq. soln. the product is always a **basic beryllium carbonate**, or **beryllium oxycarbonate.** Similar results are obtained when a soln. of a beryllium salt is precipitated with sodium or potassium carbonate, or when a soln. of beryllium hydroxide in one of ammonium carbonate, or sodium hydrocarbonate, is boiled; chemically, the basic precipitate is much the same, whether it is precipitated by the addition of a soluble carbonate, or by boiling an ammonium carbonate or dil. sodium hydrocarbonate soln. In either case, notable quantities of the precipitant are occluded, and are not all removed by washing. F. von Schaffgotsch found the basic carbonate precipitated by ammonium carbonate was not free from the double ammonium beryllium carbonate.

According to C. L. Parsons, occluded ammonia can be removed by prolonged boiling or by intermittently passing carbon dioxide through the precipitate suspended in water, filtering off the liquid and repeating. Many hours' boiling is required by the first procedure, and the residue left is almost the pure hydroxide, while if the second method is used the purification is a matter of days, but the residue is about as rich in the CO_2 component as when first precipitated. Passing carbon dioxide through the boiling liquid has little effect on the result as would naturally be expected. The ammonia may be removed with but little loss of carbon dioxide, by momentarily boiling with steam, filtering, adding fresh cold water, and repeating the operation several times. Ordinary washing with hot water does not seem to be effective. Drying at 100° does not remove the occluded ammonia, but its odour becomes immediately apparent on heating to the point where the carbon dioxide begins to be evolved.

A number of different formulæ has been reported for the basic carbonate. The proportions, $BeCO_3 : Be(OH)_2 : H_2O$, were represented by F. von Schaffgotsch as 2 : 7 : 2 ; by J. Weeren as 2 : 7 : 3 and 4 : 8 : 5 ; by H. Debray, and by G. Klatzo as 1 : 2 : 3 ; by T. Parkmann as $1 : 2 : x$; by K. Seubert and M. Elten as 1 : 5 : 3 ; and by J. H. Pollok as 1 : 2 : 2. There is here nothing to indicate that any one of these formulæ represents a chemical individual.

These reports of the composition of the basic carbonates obtained under various conditions, are themselves evidence that the different basic carbonates are merely different stages in a slow process of approach to a yet unknown condition of equilibrium in the ternary system $BeO—CO_2—H_2O$. According to C. L. Parsons, "in the presence of the largest possible amount of carbon dioxide, the composition approximates to $1 : 2 : x$, but boiling not only increases the hydrolysis, but removes carbon dioxide from the system, and slowly causes the solid phases to approach the pure hydroxide." According to F. von Schaffgotsch, the precipitate obtained by using an alkali carbonate is gelatinous and difficult to wash ; and, according to J. J. Berzelius, that obtained by boiling an ammonium carbonate soln. is granular and filters easily. According to J. H. Pollok, a litre of a sat. soln. of ammonium carbonate dissolves an amount of freshly precipitated beryllium carbonate or hydroxide eq. to 22 grms. beryllia ; and when this soln. is boiled, carbon dioxide and ammonia escape, and the white granular basic carbonate precipitate begins to appear. According to C. L. Parsons, the boiling is best done by blowing in steam, otherwise violent bumping takes place, which is not altogether prevented by continuous stirring. The basic carbonate varies in composition as the precipitation progresses ; for example, the first portions precipitated under these conditions are richer in carbon dioxide than the later precipitate, which, according to K. Seubert and M. Elten, has the composition 1 : 5 : 3 ; and if the boiling is continued until precipitation is complete, C. L. Parsons found the composition approximates to 1 : 3 : 2 (when dried over sulphuric acid) ; on the other hand, if the soln. be diluted more hydrolysis occurs with less boiling, and the composition of the precipitate approximates to $1 : 2 : x$. This product can be dried at 150° without loss of carbon dioxide. If the boiling be continued, carbon dioxide is gradually lost, and the product approximates to that of the hydroxide. C. L. Parsons attempted to increase the carbon dioxide component by passing the gas under press. over the fresh precipitate, and over the freshly precipitated hydroxide, but without success. P. N. Raikow found that freshly precipitated beryllium hydroxide absorbs enough carbon dioxide to form $BeCO_3.3Be(OH)_2$, and F. K. Cameron and W. O. Robinson measured the vap. press. of carbon dioxide over wet beryllium hydroxide at 0°, and found a slight absorption of carbon dioxide, but no evidence of the formation of a definite carbonate. The vap. press. curve in cm. of mercury approximates to a straight line :

Grms. CO_2 added . .	0·000	0·014	0·084	0·126	0·182	0·238	0·252
Vap. press. . . .	76	87	101	205	271	330	346

The basic carbonate precipitated from boiling ammonium carbonate soln. has no definite composition, but it is a convenient source for the preparation of beryllium salts because it readily dissolves in acids, and if the occluded ammonia be removed, the salts are of a high degree of purity. The substitution of sodium hydrocarbonate

for ammonium carbonate gives a precipitate less readily obtained in a granular form, and contaminated with adsorbed sodium carbonate. Both precipitates may be contaminated with a little alumina if such be present in the system. S. Meyer gave $+0{\cdot}099\times10^{-6}$ units per grm. or $0{\cdot}017\times10^{-6}$ units per mol for the magnetic susceptibility of what he regarded as $BeCO_3$; and $-0{\cdot}050\times10^{-6}$ units per grm. or $-0{\cdot}030\times10^{-6}$ units per mol for what he regarded as $BeCO_3.BeO$.

An aq. soln. of sodium carbonate was found by F. von Schaffgotsch to dissolve beryllium carbonate; if beryllia be fused with an excess of sodium carbonate, between 8·7 and 9·5 per cent. of carbon dioxide is expelled in 1½ hrs., and when extracted with water, about 77·8 per cent. of beryllia remains undissolved; that which passes into soln. is gradually precipitated by the action of atm. carbon dioxide. C. G. Gmelin found beryllium carbonate is dissolved by an aq. soln. of potassium carbonate, but beryllia precipitated from a boiling soln. of potassium hydroxide, and, according to F. von Schaffgotsch, ignited beryllia are not soluble in that menstruum. If a soln. of beryllium and potassium carbonates be boiled until the precipitate begins to form, and alcohol be then added, H. Debray found a **potassium beryllium carbonate** to which he assigned the formula $3K_2Be(CO_3)_2.Be(OH)_2$ is precipitated; it was also obtained as a white precipitate by adding alcohol to a soln. of beryllium hydroxide in potassium carbonate. If an ammonium carbonate soln. of beryllium hydroxide be treated with alcohol, the white precipitate which forms is fairly stable, and its composition depends on the relative masses of the component salts. H. Debray obtained **ammonium beryllium carbonate** by a similar process to that described for the potassium salt. The composition of the precipitate is $3(NH_4)_2Be(CO_3)_2.Be(OH)_2$, according to H. Debray, and G. Klatzo, while T. S. Humpidge assigns the formula $2(NH_4)_2Be(CO_3)_2.Be(OH)_2.2H_2O$. The product loses ammonia and carbon dioxide, slowly in the cold, but rapidly when heated.

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§ 13. Beryllium or Glucinum Nitrate

L. N. Vauquelin[1] obtained **beryllium nitrate** as an uncrystallizable elastic mass by evaporating a soln. of the hydroxide or carbonate in nitric acid. J. F. Gmelin made a similar observation as to the extreme difficulty in crystallizing the nitrate. J. M. Ordway precipitated a soln. of beryllium sulphate with barium nitrate, and evaporated the soln. over sulphuric acid. The resulting solid approached the normal trihydrated nitrate in composition, $Be(NO_3)_2.3H_2O$, but was still basic, as must necessarily occur when the salt is prepared in the presence of water in quantity. The commercial nitrate smells strongly of nitric anhydride. The aq. soln. is strongly acidic. H. Ley, and L. Bruner found that soln. with a gram-eq. per 10, 20, and 40 litres were respectively hydrolyzed 1·8, 1·8, and 1·9 per cent. at 40°. J. M. Ordway remarked on the readiness with which the nitrate loses water; at 100°, for example, its composition approximates to $2Be(NO_3)_2.BeO$. C. L. Parsons also found that by

evaporating an aq. soln. of the nitrate, it becomes strongly basic below 50°. A. Atterberg did not succeed in making the nitrate.

According to C. L. Parsons, crystals of **tetrahydrated beryllium nitrate,** $Be(NO_3)_2.4H_2O$, are easily made by saturating nitric acid with basic beryllium carbonate, evaporating to a syrupy consistency, adding conc. nitric acid in excess, and crystallizing therefrom. He added that "the crystals are highly deliquescent; they readily lose nitric anhydride, for they are stable only in the presence of conc. nitric acid, or in equilibrium with its vapour; and they melt in their own water of crystallization at 60·5°"; J. M. Ordway gave 60° for the m.p. and added that the molten liquid can be under-cooled to 34°, when it crystallizes, during which the temp. rises rapidly to about 58°. According to C. L. Parsons, the molten liquid immediately begins to give off bubbles of gas, and on raising the temp., "nitric anhydride is rapidly evolved leaving behind a viscous mass readily soluble in water when it has reached the tribasic condition. Even below 175°, it has become tetrabasic, and loses all its nitric anhydride below a red heat." He found another sample lost about 75 per cent. of its nitric anhydride when dried below 175°; and C. A. Joy found that all the nitric anhydride is evolved between 200° and 250°. C. L. Parsons found that the oxide prepared by heating the nitrate contains "a small amount of occluded oxygen and nitrogen, which, if the decomposition has been gradually brought about, is eq. approximately to 0·35 c.c. of mixed gases, of which approximately two-thirds are nitrogen, per gram of oxide." According to J. C. G. de Marignac, beryllium nitrate gives no mixed crystals with magnesium, lanthanum, or didymium nitrates. K. Jauch found the sp. ht. of N-soln. of beryllium nitrate at 18°:

N	0·5	1·0	2·0	3·0	4·0
Sp. ht.	0·9619	0·9287	0·8928	0·8443	0·7966

A. Heydweiller has measured the sp. gr., D, and equivalent conductivities, λ, of sol. containing m eq. per litre, when δD denotes the values of $(D-1)10^4$ reduced to a vacuum.

m	0·5	1·0	2·0	3·0	4·0	5·0
δD	202·4	400·9	800	1197	1592	1984
λ	63·8	56·2	45·8	37·5	30·84	24·85

According to C. L. Parsons, beryllium nitrate is insoluble in alcohol and acetone. Beryllium nitrate has been employed as a hardening agent in the manufacture of incandescent mantles.

J. M. Ordway prepared two of what he regarded as **basic beryllium nitrates,** or **beryllium oxynitrate,** the one, $3BeO.2N_2O_5$, or $2Be(NO_3)_2.BeO$, by adding beryllium hydroxide, or aq. ammonia to a soln. of the normal nitrate; and the other, $2BeO.N_2O_5.3H_2O$, or $Be(NO_3)_2.BeO.3H_2O$, by heating the normal nitrate 20 hrs. on a water-bath, or by adding beryllium carbonate to a soln. of the normal nitrate in eq. proportions. C. L. Parsons added that it is extremely doubtful if these basic nitrates are chemical compounds, but they are rather solid soln. of the normal salt and the hydroxide, or of the hydroxide with more or less occluded normal salt.

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§ 14. Beryllium or Glucinum Phosphates

The chemistry of the beryllium phosphates is not satisfactory. Comparatively few workers have studied these compounds, and the products they have described are of a gelatinous or colloidal nature, and therefore difficult to identify. It is doubtful if the normal phosphate, free from the products of hydrolysis, has been made. In 1798 L. N. Vauquelin[1] obtained a white viscid precipitate by adding an excess of disodium hydrophosphate to a soln. of a beryllium salt. The precipitate fused to a clear transparent glass, which was insoluble in water, but soluble in acids, including phosphoric acid. A. Atterberg employed the same process as L. N. Vauquelin, and obtained a white voluminous powder which he regarded as heptahydrated **beryllium orthophosphate,** $Be_3(PO_4)_2.7H_2O$; he stated that when the heptahydrate is dried at 100° nearly four mols of water were evolved, leaving behind $Be_3(PO_4)_2.3H_2O$, and he added that the product does not melt at a red heat. The phosphate dissolved in nitric acid, and, when the free acid was neutralized with ammonia, the phosphate with less combined water, was re-precipitated by treatment with sodium acetate. B. Bleyer and B. Müller obtained the hexahydrate, $Be_3(PO_4)_2.6H_2O$, by mixing acetic acid soln. of disodium hydrophosphate and beryllium sulphate; and by using normal sodium phosphate, they obtained a basic salt—**beryllium hemioxyorthophosphate,** $BeO.2Be_3(PO_4)_2.13H_2O$. F. Sestini obtained a crystalline product to which he assigned the formula $Be_3(PO_4)_2.4H_2O$, by dissolving Vauquelin's precipitate in 10 per cent. acetic acid, and boiling the filtered soln. It lost one mol of water at 100°, and the resulting $Be_3(PO_4)_2.3H_2O$ lost the remaining water at a higher temp. Sestini's phosphate dissolved in water rather more readily than aluminium phosphate; a litre of 2 per cent. acetic acid dissolved 0·55 grm., and a litre of 10 per cent. acetic acid, 1·725 grms.; the ratio $BeO : H_3PO_4$ in the soln. is the same as in the undissolved portion; and if the soln. be heated, a basic phosphate is precipitated. H. Grandeau found that beryllium and aluminium phosphates behave in a similar manner when heated with alkali sulphate—*vide infra.* G. Scheffer also obtained crystals of what he regarded as a hydrated *beryllium nitratophosphate* by concentrating a soln. of beryllium phosphate in nitric acid.

By adding alcohol to a soln. of beryllium hydroxide in phosphoric acid, A. Atterberg obtained a viscous precipitate, which gradually hardened, and to which he assigned the composition $2BeO.P_2O_5.7H_2O$, this corresponding with trihydrated **beryllium hydrophosphate,** $BeHPO_4.3H_2O$. G. Scheffer also obtained a product with a similar composition, but with less water, by adding an aq. soln. of disodium hydrophosphate to one of beryllium nitrate at 150°. B. Bleyer and B. Müller could not get the trihydrate free from adhering phosphoric acid. They prepared **beryllium dihydrophosphate,** $Be(H_2PO_4)_2$, from the hydroxide and orthophosphoric acid, in colourless hygroscopic leaflets. G. Scheffer obtained what he regarded as pentahydrated **beryllium pyrophosphate,** $Be_2P_2O_7.5H_2O$, as a white pulverulent precipitate, by adding a soln. of normal sodium pyrophosphate to one of beryllium nitrate. B. Bleyer and B. Müller gave $Be_2P_2O_7.9H_2O$ for the composition of the precipitate from sodium pyrophosphate; they also obtained colourless crystals of **beryllium metaphosphate,** $Be(PO_4)_2$. This salt must be prepared in the absence of water, or a basic salt is formed.

According to the analysis of E. S. Dana and H. L. Wells, the secondary mineral, *beryllonite,* at Stoneham (Maine), has a composition corresponding with **sodium beryllium orthophosphate,** $NaBePO_4$. It was prepared in hexagonal plates, by K. A. Wallroth, by slowly cooling a fused mixture of beryllium oxide in sodium metaphosphate and extracting the mass with water or dil. hydrochloric acid—beryllonite remains as a sparingly soluble residue. L. Ouvrard also made it in a similar way by using sodium pyrophosphate in place of the metaphosphate; he found that if normal phosphate is used, plates of **tetrasodium beryllium diphosphate** are formed: $Na_4Be(PO_4)_2$, or $Na_3PO_4.NaBePO_4$. According to E. S. Dana, native

sodium beryllium phosphate, $NaBePO_4$, forms rhombic bipyramids, with axial ratios $a:b:c=0{\cdot}57243:1:0{\cdot}54901$, and sp. gr. 2·845 at 20°; L. Ouvrard's crystals had a sp. gr. 2·72. The hardness of the mineral is $5\frac{1}{2}$ to 6 on Mohs' scale. The double refraction is negative, and the refractive indices for Na-light are $\mu_\alpha=1{\cdot}5520$; $\mu_\beta=1{\cdot}5579$; and $\mu=1{\cdot}5608$. According to K. A. Wallroth, the salt is sparingly soluble in cold acids, but easily soluble in warm acids; it is insoluble in acetic acid. Beryllonite fuses rather easily. B. Bleyer and B. Müller say that they could make sodium beryllium orthophosphate only as a precipitate of variable composition. J. Persoz stated, without giving details, that he made **alkali beryllium pyrophosphates**. According to A. Atterberg, a soln. of sodium pyrophosphate dissolves beryllium pyrophosphate; and when sodium pyrophosphate is added to a soln. of beryllium sulphate, a precipitate appears when about three-fourths of the necessary quantity of the sodium salt has been added for complete decomposition, and a gelatinous mass is finally formed. B. Bleyer and B. Müller made **sodium beryllium pyrophosphate,** $Be_2P_2O_7.2Na_4P_2O_7.5H_2O$, as a soluble hygroscopic salt.

H. Grandeau first prepared **potassium beryllium orthophosphate,** $KBePO_4$, by fusing beryllium sulphate with twenty-five times its weight of potassium phosphate between 800° and 1000°; at a higher temp. the phosphate is decomposed. The cold mass is extracted with water and rhombic prismatic acicular crystals of the double salt remain. L. Ouvrard also found rhombic prisms of the same salt are formed by fusing beryllium oxide with potassium meta-, pyro-, or ortho-phosphate. B. Bleyer and B. Müller could make potassium or ammonium beryllium orthophosphate only as precipitates of variable composition. According to C. Rössler, a crystalline precipitate of **ammonium beryllium phosphate,** similar to ammonium magnesium phosphate is produced when an excess of ammonium phosphate is added to a soln. of a beryllium salt, and the precipitate dissolved in hydrochloric acid, neutralized with aq. ammonia, and boiled. The precipitate is crystalline, and settles quickly. It is insoluble in cold water, sparingly soluble in hot water. The precipitate has a variable composition. When calcined, it loses ammonia and water, and forms beryllium pyrophosphate. M. Austin concluded that this is not an accurate way of quantitatively determining beryllium. G. Scheffer obtained a white granular precipitate of the triple salt **ammonium sodium beryllium orthophosphate,** $(NH_4)_2O.Na_2O.BeO.P_2O_5.7H_2O$, or $(NH_4)_2Na_2Be(PO_4)_2.7H_2O$, by adding disodium hydrophosphate to a soln. of beryllium nitrate, mixed with sodium chloride.

W. Haidinger [2] described a mineral which was found at the mines of Ehrenfriedersdorf, Saxony, and called **herderite**—after Brown Herder. A. Breithaupt called it *allogonite*; W. E. Hidden found a deposit at Stoneham, Maine, and called it *glucinite*. Analyses were reported by J. B. Mackintosh, C. Winkler, F. A. Genth, and S. L. Penfield and D. N. Harper. The results show that herderite is a **calcium beryllium fluo-orthophosphate**, $(CaF)BePO_4$, or rather $Ca(BeF)PO_4$, in which more or less of the fluorine may be replaced by hydroxyl. The member at the other end of the series is *hydro-herderite*, $Ca(BeOH)PO_4$. The crystals were examined by W. Haidinger, A. des Cloizeaux, W. E. Hidden, and E. Bertrand; they belong to the rhombic system, and have the axial ratios $a:b:c=0{\cdot}62060:1:0{\cdot}42345$. The optic axial angles are $2E=120°\ 33'$ to $121°\ 44'$; $2H_a=71°\ 24'$ to $70°\ 34'$; $2H_0=105°\ 11'$ to $105°\ 23'$; and $2V=74°\ 16'$ to $74°\ 29'$. The indices of refraction for Na-light are $\alpha=1{\cdot}592$, $\beta=1{\cdot}612$, and $\gamma=1{\cdot}621$. The optical character is negative. The sp. gr. ranges from 2·99 to 3·012; and the hardness is 5.

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CHAPTER XXIX

MAGNESIUM

§ 1. The History of Magnesium

In 1695, N. Grew examined the mineral water of Epsom, and, in his *Tractatus de salis cathartici amari in aquis Ebeshamensibus et hujusmodi aliis contenti natura et usu* (London, 1695), he reported his discovery of magnesium sulphate. The medicinal virtues of this salt soon afterwards became widely known, and it came to be called *Epsom salts*, *sal anglicum*, *English salts*, *sal catharticum*, *bitter salt*, etc. The presence of the same substance was detected in other mineral springs, and in 1700, G. and F. Moult established a works for extracting the salt from the waters of a spring at Shooter's Hill, near London. H. Kopp [1] says that in 1710, Mr. Hoy discovered that the same salt could be extracted from the mother liquor remaining after the evaporation of sea-water. Ferrous sulphate (colcothar of vitriol) was added, and crystallizable "bitter salt" was produced. In 1717, F. Hoffmann showed that the salt was present in the mineral waters of Seidlitz, and that derived from this source was called *Seidlitz salt*; others soon found the salt in the waters from numerous other springs.

About this time, too, T. Bergman told us, in his essay *De magnesia* (Upsala, 1775), that Count di Palma, a citizen of Rome, prepared a white powder which he claimed was a panacea for all diseases; and he induced an ecclesiastic of the Church to dispose of it for him. The powder was called *magnesia alba* or *Count Palma's powder*; and its nature was solicitously concealed as a profound secret, until M. B. Valentini disclosed the method of preparation in his *Relatio de magnesia alba, novo, genuino, polychresto et innixio pharmaco purgante Roma nuper advecto* (Giessa Hassoram, 1707), namely, by calcining the residue remaining after evaporating to dryness the mother liquor from the preparation of nitre. We are also told that two years later J. H. Slevogt [2] showed how *magnesia alba* could be more easily obtained by precipitation from the mother liquors by treating them with a fixed alkali. Works by B. J. Lembcken,[3] H. Smith, S. Glass, D. Ingram, J. Schaeffer, C. Norell, P. J. Macquer, and T. Henry are of historical interest.

It is not known why the name *magnesia alba* was given to the product in contrast with *magnesia nigra*, as the black oxide of manganese was then called. Dioscorides used the terms μάγνης λίθος or μάγνης, and Pliny *magnes*, for magnetic iron ore and pyrolusite. According to the latter:

> It received its name magnes, Nicander informs us, from the person who was the first to discover it upon Ida. (Isodorus, in his *Origines*, said India.) It is said that Magnes made this discovery when, upon taking his herds to pasture, he found that the nails of his shoes and the iron ferrule of his staff adhered to the ground.

Others refer the terms to the place where the stone was found—*e.g.* Magnesia in Asia. Pliny distinguished between what he called the male and female sex of magnes—*magnes qui niger est feminei sexus ideoque sine viribus*, and he described five different kinds of *magnes*, all but one of which were nearly black. The magnes from Magnesia in Asia was said to be white, and to resemble pumice in appearance, but to have no attractive influence on iron. From the early writings it is evident that at least three minerals of a totally different nature were called magnesia—(i) *magnesius lapis*, which is now represented by magnetite, was magnetic;

(ii) *magnesia nigra*, which is now represented by pyrolusite ; and (iii) a silver-white mineral, which could be conveniently fashioned in a lathe, or easily shaped and carved with hand tools, and it is probably now represented by steatite.

The alchemists used the word magnesia in a number of different senses. It was their custom to appropriate common terms and give special meanings associated with their mystical notions. Thus A. E. Waite [4] says :

> Magnesia was at different times the matter, red or white, of the philosopher's stone ; something like common mercury, of celestial and transcendent brightness ; neither animal, vegetable, nor mineral ; resembling a stone but not a stone ; white gum ; water of the sea ; water of life ; child of the elements ; a pure virgin ; a secret celestial spirit, neither thick nor thin, not wholly earthy nor wholly igneous, but a mean aerial substance, to be found everywhere and at all seasons.

J. Beckmann has said that the term *manganese* is a corruption of the word magnesia, and that it was first used by Albertus Magnus who, in his *De mineralibus*, wrote the name of the magnet in at least five different ways : *magnesia*, *magnasia*, *magnosia*, *mangadesum*, and *manganensis*. The difference between *magnesia nigra* and the magnetic ore was demonstrated towards the middle of the eighteenth century. At the beginning of that century Count di Palma's powder appeared, and the French, English, and Italians soon afterwards employed the term *manganes* for the black mineral and *magnesia* for the white. Thus, in the sixteenth century, C. Leonard,[5] M. Mercati, and H. Cardan employed the term *manganes* for *magnesia nigra*, although metallic manganese was not discovered until the eighteenth.

F. Hoffmann, in his *Dissertationum physico-chymicarum* (Halæ Magdeburgicæ, 1729), first demonstrated the individuality of magnesia which had long been confounded with lime. Speaking of Epsom salts, he said :

> There are a great number of waters—among which may be cited these of Eger, Elster, Schwalbach, and Wildung—containing a neutral salt which has not yet received a name, and which is almost unknown. I have found it in the waters of Hornhausen, which owe to this salt their apertive and diuretic properties. It is commonly called *nitrum*, but it has none of the characters of nitre—*e.g.* it is not inflammable, its crystalline form is different, and it does not give aqua fortis like nitre does. It is a neutral salt resembling *arcanum duplicatum* (potassium sulphate), its taste is bitter, and it produces with the tongue a sensation of cold ; it effervesces neither with acids nor alkalies, and is not very fusible. . . . This salt appears to have been formed *ex combinatione acidi sulphurei et calcaria terra* of an alkaline nature.

A few years later, F. Hoffmann returned to the subject in his *Observationum physico-chymicarum* (Venetiis, 1740), and added that the alkaline earth prepared by treating bitter salt with a fixed alkali, differs essentially from lime, in that when the latter is treated with sulphuric acid, it gives a sparingly soluble salt, which does not taste bitter, and is nearly without taste. Hence bitter salt is composed of sulphuric acid and a kind of alkaline calcareous earth which is different from lime. J. Black, in his paper entitled *Experiments upon magnesia alba, quick-lime, and other alcaline substances* (Edinburgh, 1755), also showed that *magnesia alba* is a compound of fixed air (carbon dioxide) with a peculiar earth which differed from lime in furnishing a soluble sulphate ; and he retained for this new earth the name *magnesia*. In Germany the terms *Bittersalzerde*, *Bittererde*, and *Talkerde* were employed. The properties of magnesia were described in more detail by A. S. Marggraf [6] (1759), and by T. Bergman. E. Nauck, L. C. Marquart, and J. J. Nöggerath discuss the occurrence of magnesium metal in old bronzes.

B. G. Sage may have obtained the metal base of magnesia in 1777, for he described the following experiment with Epsom or Seidlitz salts :

> One ounce of the salt was dissolved in distilled water, and treated with *huile de tartre*—potassium carbonate which had become liquid by deliquescence—the resulting white precipitate was washed, dried, and then mixed with three times its weight of powdered charcoal. The mixture was luted in a glass vessel, and heated for three hours in a reverberatory furnace. The vessel was allowed to cool, and then broken. Mixed with the charcoal were found small, grey, fragile metallic globules which he supposed to be zinc ; but he

stated that the quantity obtained was insufficient for proof, but he said that the metal alloyed with copper formed a brass.

In 1808, H. Davy definitely proved that magnesia is the oxide of a metal which he named *magnium*, and added that this word "is undoubtedly objectionable, but magnesium was employed by T. Bergman for metallic manganese, and would consequently have been an equivocal term." The term magnesium was soon afterwards reserved for the metal in magnesia alba, and manganese for that in pyrolusite. For a time some chemists called magnesium, *talcium*. J. B. Trommsdorff discussed the metal derived from Talkerde in 1828.

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§ 2. The Occurrence of Magnesium

Magnesium metal does not occur free in nature. This element is considered to be abundantly distributed on the earth's crust. According to F. W. Clarke's estimate,[1] it occupies 8th place in the list of elements arranged in the order of decreasing abundance in the earth's lithosphere, and there is 2·24 per cent. of that element present. The distribution of magnesia in the lithosphere is:

	Igneous (95%)	Shale (4%)	Sandstone (0·75%)	Limestone (0·25%)	Average
MgO	3·74	2·44	1·16	7·89	3·74

N. Ljubavin has also made an estimate of the relative distribution of magnesium on the earth's crust. F. Cornu, and C. A. Young have reported the lines of magnesium in the solar spectrum. G. Rayet, C. Fievez, W. N. Hartley, and A. Secchi found the lines of magnesium in the spectra of the solar protuberances; also in the spectrum of Hercules.

Magnesium occurs as the oxide, *periclase*, MgO; and as the hydroxides *brucite*, $Mg(OH)_2$; *hydrotalcite* or *völkerite*, $3Mg(OH)_2.Al(OH)_3.3H_2O$; and *pyroaurite*, $3Mg(OH)_2.Fe(OH)_3.3H_2O$. There is also the aluminate: *spinel*, $Mg(AlO_2)_2$; *magnesioferrite*, $Mg(FeO_2)_2$; as well as the aluminoferrites: *pleonaste* or *iron spinel*, $(Mg,Fe)\{(Al,Fe)O_2\}_2$; *picotite* or *chromospinel*, $(Mg,Fe)\{(Al,Fe,Cr)O_2\}_2$; and *manganospinel*, $(Mg,Mn)\{(Fe,Mn)O_2\}_2$. Magnesium is widely distributed among the silicate minerals (*q.v.*), the commonest of which are *talc*, *chlorite*, and *serpentine*. It is represented by amphiboles, pyroxenes, micas, and olivine in the igneous rocks. There are enormous deposits of the carbonate: *magnesite*, $MgCO_3$; and *dolomite* or *bitter spar*, $(Mg,Ca)CO_3$. In addition there are: *brown spar* or *ankerite*, $(Ca,Mg,Fe,Mn)CO_3$; *breunerite*, $(Mg,Fe)CO_2$; and *nesquehonite*, $MgCO_3.3H_2O$;

and the basic carbonates: *hydromagnesite*, $Mg_2(OH)_2(CO_3).3H_2O$; and *lansfordite*, $Mg_2(OH)_2CO_3.21H_2O$. The haloid salts are represented by *sellaite*, MgF_2; *bischofite*, $MgCl_2.6H_2O$; *carnallite*, $MgCl_2.KCl.6H_2O$; *nocerite*, $(Mg,Ca)_3OF_4$; *ralstonite*, $(Na_2,Mg)F_2.3Al(F,OH)_3.2H_2O$; and *tachhydrite*, $2MgCl_2.CaCl_2.12H_2O$. Some mineral springs in Java contain magnesium iodide, MgI_2, eq. to 0·012 grm. per litre. The sulphates are represented by: *astrakanite*, *blödite* or *simonyite*, $Na_2Mg(SO_4)_2.4H_2O$; *botryogen*, $(FeOH)_4(Mg,Fe,Mn,Ca)_5(SO_4)_9.36H_2O$; *cupromagnesite*, $(Cu,Mg)SO_4.7H_2O$; *dumreicherite*, $Mg_4Al_2(SO_4)_7.36H_2O$; *epsom salts* or *epsomite*, $MgSO_4.7H_2O$; *fauserite*, $(Mg,Mn)SO_4.7H_2O$; *kainite*, $MgSO_4.KCl.3H_2O$; *kieserite*, $MgSO_4.H_2O$; *klinophaite*, $(Fe,Al)_2(Fe,Mg,Ni,Ca)$-$(K,Na)_2(OH)_6(SO_4)_5.5H_2O$; *krugite*, $K_2Ca_4Mg(SO_4)_6.2H_2O$; *löwite*, $Na_2Mg(SO_4)_2.2\frac{1}{2}H_2O$; *magnesia alum*, or *pickeringite*, $MgAl_2(SO_4)_4.22H_2O$; *melanterite*, $(Mg,Fe)SO_4.7H_2O$; *picromerite*, or *schönite*, $K_2Mg(SO_4)_2.6H_2O$; *plagiocitrite*, $(Al,Fe)_3(Fe,Mg,Ni,Ca)(K,Na)$-$(OH)_6(SO_4)_3.21H_2O$; *polyhalite*, $K_2Ca_2Mg(SO_4)_4.2H_2O$; *sonomaite*, $Mg_3Al_2(SO_4)_6.33H_2O$; *voltaite*, $(Fe,Al)_4(Mg,Fe,K_2,Na_2)(OH)_2(SO_4)_{10}.14H_2O$; *wattevillite*, $(Na,K)_2(Ca,Mg)(SO_4)_2$-$2H_2O$. There is the nitrate, *nitromagnesite*, $Mg(NO_3)_2$; and a series of phosphates, arsenates, borophosphates, and borates: *Berzeliite*, $(Ca,Mg,Mn,Na_2)_3(AsO_4)_2$; *bobierrite*, $Mg_3(PO_4)_2.8H_2O$; *boracite*, $Mg_7Cl_2B_{16}O_{30}$; *boromagnesite*, $4Mg(BO_2)OH.Mg(OH)_2$; *cabrerite*, $(Ni,Mg,Co)_3(AsO_4)_2.8H_2O$; *hannayite*, $Mg_3(NH_4)_2H_4(PO_4)_4.8H_2O$; *hörnesite*, $Mg_3(AsO_4)_2$-$8H_2O$; *hydroboracite*, $MgCaB_6O_{11}.6H_2O$; *karyinite*, or *caryinite*, $(Mn,Ca,Pb,Mg)_3(AsO_4)_2$; *lazulite*, $(AlOH)_2(Mg,Fe,Ca)(PO_4)_2$; *lüneburgite*, $2MgHPO_4.Mg(BO_2)_2.7H_2O$; *martinite*, $Ca_5H_2(PO_4)_4.\frac{1}{2}H_2O$; *newberyite*, $MgHPO_4.3H_2O$; *picropharmacolite*, $(CaMg)_3(AsO_4)_2.6H_2O$; *pinnoite*, $Mg(BO_2)_2.3H_2O$; *roselite*, $(Ca,Mg,Co)_3(AsO_4)_2.2H_2O$; *rösslerite*, $MgHAsO_4.\frac{1}{2}H_2O$; *struvite*, $Mg(NH_4)PO_4.4H_2O$; *sussexite*, $(Mg,Zn,Mn)(OH)BO_2$; *wagnerite*, $Mg(MgF)PO_4$; *wapplerite*, $(Ca,Mg)HPO_4.3\frac{1}{2}H_2O$. There is also a number of silicates (*q.v.*).

The waters of numerous springs as a rule contain small quantities of magnesium compounds which appear in the analyses as magnesium sulphate, chloride, or hydrocarbonate; sea-water also contains magnesium which appears in F. W. Clarke's average analysis of oceanic salts as magnesium chloride, 10·88; magnesium sulphate, 4·74; magnesium bromide, 0·22; together with sodium chloride, 77·76; calcium sulphate, 3·60; calcium carbonate, 0·34; and potassium sulphate, 2·46 per cent. The waters of the Dead Sea contain more magnesium chloride than sodium chloride. F. W. Clarke estimates that on the average 0·14 per cent. of magnesium is contained in the waters of the earth.

According to R. Willstätter,[2] magnesium is an integral part of chlorophyll; and J. Kacher considered it to be an indispensable constituent of plants, saccharomyces, etc.; the ashes of plants usually contain more calcium than magnesium, although the reverse is true for seeds. It is not known how the magnesium is distributed in the organs of plants, but it occurs in the cambium sap of pines as oxalate. R. Kayser found that the amount of magnesium in wine is proportional to the phosphoric acid, and that the smallest amount—0·001 per cent. MgO—was found in Pfälzer wine, and the greatest amount—0·040 per cent. MgO—in Malaga wine. Magnesium compounds also accompany the calcium compounds in animal bodies; and magnesium salts occur in the skeleton, blood, and milk of animals. F. W. Clarke and W. C. Wheeler found it very exceptional for the inorganic parts of sea organisms to be non-magnesian. They found the following percentage amounts in the inorganic matter: Foraminifera, 3·67–11·22; calcareous sponges, 5·37–8·00; madreporian corals, 0·09–0·77; alcyonarians, 6·03–15·73; hydroids, 0·22–1·28; annelids, 0·00–9·72; echinoderms, 5·99–14·08; brachiopods, 0·49–8·63; bryozoans, 0·63–11·08; molluscs, 0·00–2·58; barnacles, 0·79–2·49; and other crustaceans, 4·84–15·99.

A comparison of rock and other analyses makes it probable that the solid crust of the earth contains more calcium than magnesium. Analyses of meteorites reveal more magnesium than calcium; the same remark applies to sea-water, most mineral waters, and lakes in Central and North-Western Asia. Calcium prevails in river waters, in most plants and in animals; some cereals contain more magnesium.

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§ 3. The Preparation of Magnesium

Magnesium is usually obtained by the action of sodium on the anhydrous chloride, or by the electrolysis of fused alkali-magnesium chloride. The magnesium chloride was formerly obtained from Stassfurt, but during the 1914–18 war, it was recovered as a by-product at various salt works. It is used as a powder and ribbon for flash-lighting ; as a deoxidizer of other metals and alloys ; and in making certain alloys—principally Mg–Al alloys. Magnesium occurs in commerce as powder, ribbon, and as ingots or rods. The ribbon is made by pressing the metal in the semi-fluid state into wire ; and afterwards flattening it into ribbon by rolling.

The reduction of magnesium oxide.—H. Davy passed the vapour of potassium over red-hot magnesium oxide, and removed the magnesium produced by mercury. J. Walter [1] tried to reduce magnesium oxide by carbon under the conditions which obtain in the manufacture of zinc. The experiments were conducted at low redness and at a white heat, and precautions were taken to isolate the metal, if formed, whether distilled or volatilized. His results were negative, although he considered it would be possible to prepare a kind of *magnesium brass*, *i.e.* a Mg–Zn alloy, by substituting some dolomite for the zinc ore ordinarily used in the manufacture of zinc. E. von Püttner, however, claimed to have made magnesium by heating burnt magnesite, dolomite, or other magnesian mineral mixed with coal and ferric oxide, and by exposing to a strong white heat in a muffle furnace as in the process for zinc extraction. The vapour of magnesium was condensed in suitable receivers. E. D. Clarke said that when magnesia is mixed with oil, and exposed to the oxy-hydrogen flame, a slag is obtained which crumbles to white pulverulent magnesia when exposed to the air. It will be observed that the possible products of the deoxidation in the reduction of magnesia by carbon : $n\mathrm{MgO}+(n-\frac{1}{2}m)\mathrm{C}=n\mathrm{Mg}+(n-m)\mathrm{CO}+\frac{1}{2}m\mathrm{CO_2}$, are both reduced by the magnesium at a high temp. H. Moissan claimed that " magnesia can be fused, and kept liquid in a carbon crucible without being reduced." P. Lebeau considers that a reaction occurs only between the vapours of carbon and magnesia at the high temp. of the electric arc. R. E. Slade found that the metal can be isolated from a mixture of carbon and magnesia provided the reoxidation of the magnesium by the carbon monoxide is prevented by rapidly removing this gas, say, by working in vacuo, or by absorbing the magnesium by another metal, or by a rapid stream of hydrogen. The condensed magnesium is always associated with a little carbide which gives off acetylene when treated with a dil. acid or water. O. P. Watts also volatilized carbon from a bed of magnesia, and obtained sublimates consisting of mixtures of carbon and magnesium oxide. O. P. Watts found that at very high temp. magnesia and carbon react : $\mathrm{MgO}+\mathrm{C}\rightleftharpoons\mathrm{CO}+\mathrm{Mg}$, and at a lower temp. the reaction is reversed. O. L. Kowalke and D. S. Grenfell found the reduction of magnesia by carbon begins slowly at 1950°, and becomes violent at 2030°. C. Matignon studied the preparation of magnesium by reducing magnesium oxide, magnesium chloride or oxychloride with calcium carbide. O. Knöfler and H. Ledderboge made rods of magnesia and carbon, and used them as the electrodes of an electric arc. To avoid the action of the products of combustion of carbon on the metal, the arc was developed in vacuo, or in an indifferent gas. J. Malovich mixed the oxide, or a salt of magnesium with sulphur and the sulphate or sulphite of another metal, and heated the mass to a temp. above the m.p. but below the volatilization temp. of the metal or alloy to be obtained.

The reduction of magnesium halides by the alkali metals.—A. A. B. Bussy first prepared magnesium as a coherent metal in 1829 by decomposing red-hot anhydrous magnesium chloride by potassium vapour, following the process previously employed by F. Wöhler for aluminium. J. von Liebig employed the same process. According to R. Bunsen, magnesium reduced with potassium retains a little of the latter metal very tenaciously, and the resulting metal is more malleable than magnesium free from potassium. H. St. C. Deville and H. Caron improved the process, substituting sodium for potassium. They heated the mixture: magnesium chloride, 7 parts; calcium fluoride, 4·8 parts; and sodium, freed from oil, 2·3 parts to bright redness in a clay crucible—E. Sonstadt used an iron crucible. The magnesium which separated in globules was heated nearly to whiteness in a carbon boat placed in an inclined tube of the same material and through which a stream of dry hydrogen was passed. The magnesium which condensed in the upper portion of the tube was melted into large globules with a flux made of calcium fluoride and sodium and magnesium chlorides. They obtained a yield of 45 grms. of magnesium from 100 grms. of sodium. According to H. St. C. Deville and H. Caron, and E. Sonstadt, the metal prepared by the sodium reduction process contains carbon and silicon as impurities, and, if ammonium chloride is present, some magnesium nitride, Mg_3N_2, as well. To remove carbon, silicon, and nitrogen, H. St. C. Deville and H. Caron distilled the metal in a current of hydrogen at a high temp. According to J. B. A. Dumas, the metal usually contains two-thirds of its volume of occluded hydrogen and a little carbon monoxide, which are removed by heating it in vacuo at a red heat. E. Sonstadt improved the distillation apparatus. The crude metal was placed in an iron crucible fitted with an iron tube passing through the bottom to within an inch of the lid. The crucible was nearly filled with the crude metal; the lid screwed and luted down; and the air displaced by coal gas or hydrogen. When the crucible was heated, the vapour of magnesium passed into the upright tube and, by a process of *distillation per descensum*, collected as a coherent mass in a box placed below. The metal was then melted and cast into ingots. F. Wöhler applied the sodium reduction process to a fused mixture of sodium and magnesium chlorides; A. Matthiessen, to a mixture of magnesium and potassium chlorides with a little ammonium chloride; H. Schwarz, to tachhydrite; C. Tissier, to sodium magnesium fluoride; and E. Reichardt, to carnallite. The latter used a mixture of equal parts of previously fused carnallite, calcium fluoride, and sodium; and he said that ferruginous mica in the carnallite does no harm, but the presence of kieserite is to be avoided since an explosion may be produced when it is present.

F. Lauterborn heated magnesium ferrocyanide with sodium carbonate so as to produce a double cyanide of magnesium and sodium from which the magnesium was obtained by heating it with zinc. T. Petitjean proposed to reduce magnesium sulphide by iron, or by hydrocarbon vapours at a red heat. M. Basset patented a modification of this process.

The electrolysis of aqueous solutions of magnesium salts.—H. Davy tried to make magnesium by the electrolysis of moistened magnesium hydroxide or sulphate with a mercury cathode and subsequently distilling off the mercury, but the results were bad. A. C. Becquerel electrolyzed a conc. soln. of magnesium chloride in the cathode compartment, and a conc. soln. of sodium chloride in the anode compartment of an electrolytic cell. Octahedral crystals deposited on the cathode. F. W. Gerhard and J. Smith electrolyzed a soln. of 228 parts of magnesium sulphate and 132 parts of ammonium sulphate in 35,000 parts of water between 65° and 100°. For an alloy of magnesium and nickel, a nickel anode was used; for magnesium bronze, a copper anode was used and potassium cyanide and ammonium carbonate were added to the electrolytes. M. Rietz and M. Herold prepared a soln. of magnesium oxide or carbonate in an organic acid, to which was added starch or gum, the soln. boiled with sugar, and neutralized with alkali. This was electrolyzed. If alloys of magnesium are required, a cyanide of the required metal is added to the electrolyte, and an anode of that metal used. G. Nahnsen and J. Pfleger have patented a

special electrolysis cell; and H. Decker, the use of a mercury cathode. The production of magnesium by the electrolysis of aq. soln. has not been successful; nor has the electrolysis of soln. of magnesium salts in non-aq. solvents yet proved of practical utility.

The electrolysis of fused magnesium salts.—In 1852, R. Bunsen [2] prepared magnesium by the electrolysis of magnesium chloride fused in a porcelain crucible. The carbon of the negative electrode was cut to form pockets in which the metal collected, otherwise, the metal, being lighter than the fused chloride, rose to the surface and burned. There is a difficulty in preparing magnesium chloride, for, when an aq. soln. of the salt is evaporated to dryness and fused, the residue contains magnesium oxide, owing to the hydrolysis of the salt and the escape of hydrogen chloride. A. Matthiessen preferred, as electrolyte, a fused mixture of $3KCl+4MgCl_2$, with a little ammonium chloride. The magnesium in this case is largely present as a complex anion, and hydrolysis does not occur so readily. A great deal of commercial magnesium is obtained by the electrolysis of fused carnallite. F. Fischer first recommended the use of an electrolyte of fused carnallite, and showed that the combustion of the magnesium can be prevented by passing a current of a reducing gas over the electrolyte. In R. Grätzel's apparatus, Fig. 1, the iron vessel *A* contains the fused electrolyte, heated externally, and sealed by a lid through which pass the tubes *TT'*, which allow a stream of a reducing or inert gas to be passed over the molten electrolyte, thus protecting the magnesium from oxidation. The vessel *B* has openings *CC* to allow the circulation of the molten electrolyte, and is fitted with a carbon anode, from which chlorine is liberated during the electrolysis. W. Borchers, F. Hornung and F. W. Kasemeyer, E. Haag, etc., have investigated this mode of preparation. According to R. Bunsen, the metal prepared by electrolysis usually contains a very small proportion of aluminium and silicon.

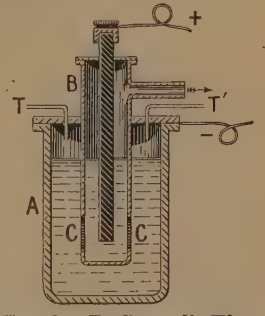

Fig. 1.—R. Grätzel's Electrolytic Cell for Magnesium (Diagrammatic).

Magnesium melts at about 633°; magnesium chloride at about 708°; and carnallite at a lower temp. S. A. Tucker and F. L. Jouard attempted to work at 500°, when the metal is produced in a spongy form which is subsequently melted under a flux of calcium chloride and electrolyzed. According to A. Oettel, the best working temp. is about 650°, for then the efficiency of the process is greatest; but by working at that temp. it is difficult to keep the temp. sufficiently constant to prevent the solidification of the magnesium, and therefore A. Oettel recommended 700°–750°; and W. Borchers, 700°. A. Oettel worked at 4–8 volts, W. Borchers at 5–8 volts—depending on the current density and temp. The decomposition voltage of magnesium chloride is estimated to be less than 3·2 volts at 700°, and, assuming that this number represents the value for carnallite, the energy efficiency for a current efficiency of 75 per cent. and 6 volts, is $75\times\frac{1}{6}$ of $3{\cdot}2=40$ per cent.; and a kilogram of metal requires $(1000\times2\times96540\times100\times6)\div(24{\cdot}3\times75\times3600\times1000)$ or 17·7 kilowatt-hrs. A. Oettel showed that the presence of calcium fluoride as a flux favours the coalescence of the globules of magnesium formed at the cathode. If the globules do not coalesce, but pass into the electrolyte, they form a metal fog about the anode, when they are reoxidized. If the carnallite is contaminated with ferric chloride, losses occur owing to the continuous reduction of this salt at the cathode and its reoxidation at the anode. If too high a voltage is used, or if the magnesium chloride content of the bath becomes too low, the magnesium may contain some potassium, and it is then liable to catch fire during the electrolysis. E. Hohler studied the electrolysis of a molten mixture of equi-molar proportions of magnesium, potassium, and sodium chlorides, along with calcium fluoride and a little alkali to keep the electrolyte sufficiently basic. The best working temp. was 750°–800°, and a 70 per cent. current efficiency was obtained. The cathodic

current density of 27–30 amps. per sq. dm. was used ; W. Borchers used 10 amps. per sq. dm. ; and A. Oettel, 30–40 amps. per sq. dm. The subject has been discussed by S. T. Allen, and by K. S. Boynton and co-workers.

According to R. Lorenz and F. Kaufler, some magnesium is produced by the contact electrode process—*vide* Fig. 1 in connection with the preparation of calcium. A. Oettel has shown that the resulting rod of magnesium is somewhat brittle ; and, owing to the need for high current densities, the potassium content is liable to rise. M. Sprenger removed the chlorine under reduced press. H. M. A. Berthaut used an electrolyte of magnesium and sodium chlorides ; A. Feldmann, a mixture of alkali magnesium chloride mixed with some calcium oxide ; F. von Kügelgen and G. O. Seward, magnesium oxide dissolved in fused magnesium fluoride and an alkali fluoride ; and the latter also used a bath of fused magnesium and calcium chloride with some calcium fluoride ; J. T. Morehead, magnesium fluoride or fluoride and chloride mixed with one, two, or more chlorides of the alkali metals. Magnesium alloys can be made directly by electrolyzing a fused bath of magnesium chloride and fluoride with a carbon anode, and an aluminium cathode. This forms a magnesium-aluminium alloy which can be used as a stock in making alloys of any desired composition—*e.g.* F. von Kügelgen and G. O. Seward's process.

T. Svedberg [3] prepared **colloidal magnesium** by connecting a glass condenser of 225 sq. cm. surface with the induction coil and attaching the secondary poles to the electrodes, which are immersed in propyl or isobutyl alcohol contained in a porcelain dish. The magnesium was used in a granular form or as wire clippings. When the current is passed, sparks play between the metal particles, and in the course of a few minutes dark-coloured soln. are obtained. These contain no large particles, and hence need not be filtered. The magnesium sol in absolute ether is olive-green, and very readily coagulated ; the coagulum is greenish-black, and very vigorously dissolved by dil. acids with the evolution of hydrogen. D. Zavrieff used a modification of T. Svedberg's process, and obtained a colloidal soln. which could be kept two days without flocculation.

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§ 4. The Physical Properties of Magnesium

The magnesium prepared by A. A. B. Bussy [1] was a brilliant silver-white metal, and that by H. St. C. Deville and H. Caron had a bluish or violet tinge. According to A. W. Wright, the metal volatilized in an evacuated tube by means of an electric discharge, produces a metallic film which is silvery-white in reflected light, and greyish-blue by transmitted light. R. Bunsen noted that the metal has a crystalline fracture. S. Kalischer could detect no crystals structure by etching the rolled metal, and he found that although most metals naturally have a crystalline structure, some readily lose this structure by mechanical processes, but assume it again under the influence of heat. According to C. Hlawatsch, and A. des Cloizeaux, the **crystals** prepared by J. B. A. Dumas, by sublimation in a stream of hydrogen, are hexagonal prisms, $a : c = 1 : 1{\cdot}6242$. These crystals have also been studied by E. Bamberger, and L. Ditscheiner. Regular hexagons were obtained by etching with dil. sulphuric acid, or with chlorine. Z. Jeffries and R. S. Archer give 150° as the lowest temp. at which the recrystallization of the cold-worked metal has been observed. G. T. Beilby showed that the crystalline structure of the metal is hidden when the surface is polished owing to the formation of an amorphous glass-like film which can be removed by an etching liquid. L. Hamburger made an ultra-microscopic examination of these films of the metal. **X-ray spectrograms,** by A. W. Hull, and H. Bohlin, showed a structure in agreement with the holohedral hexagonal crystals. The arrangement of the atoms is that of hexagonal close packing, that is, the arrangement which equal hard spheres assume when closely packed, except that the structure is shortened by about 0·5 per cent. in the direction of the hexagonal axis. The side of the hexagonal lattice is 3·22 A., height 5·23 A., and the closest approach of the atoms is 3·22 A. As in the face-centred cubic lattice, each atom has twelve equidistant near neighbours, but in a slightly different arrangement. G. Jäger made an estimate of the **molecular diameter** of magnesium; W. L. Bragg gave $0{\cdot}142\mu\mu$ or 1·42 A. for the radius of the atomic spheres; M. N. Saha, 0·95 A.; K. F. Slotte estimates the edge of the molecular cube of the liquid and solid to be $7{\cdot}3\times10^{-9}$ cm. C. T. Heycock and F. H. Neville estimated the **molecular weight** of magnesium in soln. in lead, and tin. K. Honda and S. Konno gave $1{\cdot}61\times10^{8}$ for the coeff. of normal **viscosity** of hammered magnesium at 20°; and $0{\cdot}722\times10^{8}$ for the metal annealed at 400°. G. P. Seaman studied the torsional oscillations of magnesium wire between −180° and 500°, and found very little change. C. E. Guye and co-workers measured the effect of temp. on the viscosity of magnesium.

L. Playfair and J. P. Joule's value 2·24 (3·9°) for the **specific gravity** of magnesium is too high, and must have been made on an impure sample. R. Bunsen's value is 1·7430 at 5°; H. Kopp's, 1·70 at 17°; H. St. C. Deville and H. Caron's value, 1·75; and H. Wurtz's value, 1·77 at 0°. T. M. Lowry and R. G. Parker found the sp. gr. of purified magnesium was raised from 1·7381 to 1·7429 on filing. This is not usual, the filings, like worked metals, usually have the lower sp. gr. When partially annealed at 180°, they expand, but contract if further annealed at 240°. The at. vol. of magnesium does not fit very well in series with the other elements of the magnesium family, and in this respect, this element fits in better with the calcium family. R. Bunsen found the **hardness** of magnesium to be almost equal to that of calcite. C. A. Edwards gave 38·3 for Brinell's hardness. The subject has been discussed by P. Ludwik, and A. Kürth. A. A. B. Bussy said the metal can be hammered into thin sheets; J. von Liebig, and R. Bunsen found that it can be filed,

and bored, and that at ordinary temp. the **ductility** is scarcely as great as that of zinc. H. St. C. Deville and H. Caron stated that while the crude metal is brittle, purified magnesium is very ductile, and while it cannot be drawn into wire, it can be converted into wire by press. through a die. W. Böhm obtained magnesium foil by rolling the metal at a temp. just below its m.p. J. W. Buchanan found the linear **compressibility** to be $1{\cdot}054\times10^{-6}$ dynes per sq. cm., or 3·2 kgrms. per sq. cm., per atm. press. between 7° and 12°. T. W. Richards and co-workers found the average compressibility, that is, the fractional change of volume caused by one megabar press. between 100 and 500 megabars, to be $2{\cdot}7\times10^{-7}$. W. Sutherland gave 390×10^{-6} grms. per sq. cm. or 3900 kgrms. per sq. mm. for **Young's modulus** or the **modulus of elasticity** at 15°, with the extremes 3520 and 4310 kgrms. per sq. mm. W. Voigt's value for the modulus of elasticity of cast magnesium is 4260 kgrms. per sq. mm. P. Ludwik made some observations on the tensile strength of magnesium. C. J. Burton and W. Marshall observed a rise of 0·00047° per atm. increase of press.

According to W. Sutherland, the ratio of the **rigidity** or torsion modulus at 100° to the value at zero is 0·943, and his value for the absolute value in kgrms. per sq. mm. is 1300; H. Tomlinson's, 1720; C. Schäfer's, 1181; W. Voigt's value for the cast metal is 1710, with a change of —30 per cent. per 100° rise of temp. F. Melde found the **velocity of sound** in magnesium to be 4602 metres per second.

E. Grüneisen[2] found the **coefficient of linear expansion,** α, of magnesium between —190° and 17° to be 0·00002130; and from 17° to 100°, 0·00002610, or 0·0000250 at 18°; and for the expansion from absolute zero to the m.p., T_s° K., he gave 0·0248 or $0{\cdot}00000277T_s^{1\cdot337}$, where T_s=903° K. K. Scheel found the linear expansion of magnesium between 0° and θ° to be

	0°	100°	200°	300°	400°	500°	
δl . . .	0	2·60	5·39	8·36	11·53	14·88	mm. per metre

and he represented the results by $\delta l=0{\cdot}02507\theta+0{\cdot}00000936\theta^2$. J. Desch made some observations on the expansion of magnesium at temp. down to —190°. R. Bunsen said magnesium melts at a red heat, and H. St. C. Deville and H. Caron that it melts near the m.p. of zinc. The reported values for the **melting point** of magnesium range from the 500° of A. Ditte to the 800° of V. Meyer; C. T. Heycock and F. H. Neville gave 632·5°–632·8°; G. Grube, 650·9°; S. F. Schemtschuschny, and R. Vogel, 649°; C. H. Mathewson, G. G. Urasoff, and P. Sahmen, 650°; G. Voss, and N. S. Kurnakoff and N. J. Stephanoff, 651°; N. Beer, 632·6°. According to W. Guertler and M. Pirani, the best representative value is 651°. F. Wöhler noted the volatility of magnesium, and H. St. C. Deville estimated that the **boiling point** is near that of zinc, A. Ditte said about 1100°. H. C. Greenwood gave 1120° for the b.p., while H. von Wartenberg gave a value over 1200°. V. and A. Meyer stated that the metal does not volatilize at a white heat in an atm. of carbon monoxide; while H. Cretier said that volatilization begins below the m.p.; and W. C. Roberts-Austen said that the metal has an appreciable vap. press. at ordinary temp. G. Bartha obtained a partial evaporation of magnesium in vacuo at 580°. H. St. C. Deville and H. Caron purified the metal by distillation, and obtained a black crystalline residue of magnesium nitride. J. B. A. Dumas obtained good crystals by sublimation in vacuo at a red heat. A. Schuller noted that the molten metal attacks glass, and C. Margot found that the adhesion of molten magnesium to glass is due to the formation of a film of oxide on the metal, and that the film can be removed by rubbing. M. Knudsen found that the condensation of the vapour of magnesium on a clean glass or mica surface, has a critical temp., —183° to —78°, below which all the vapour is retained, and above which a fraction is repelled. J. W. Richards estimated the latent **heat of fusion** to be 58 cals.; and the latent **heat of vaporization** 31·580 cals. per mol., or 1315 cals. per kilogram. E. van Aubel, and A. Wehnelt and C. Musceleanu observed 1700 cals. per mol. H. V. Regnault gave 0·2499 for the **specific heat** of magnesium, containing 0·06 per

cent. of silicon and 0·08 per cent. of aluminium and iron. H. Schimpff found over the range −190° to 100°, and N. Stücker, over the range 20° to 650° :

	−190° to 17°	−79° to 17°	17° to 100°	20° to 100°	20° to 350°	20° to 650°
Sp. ht. . . .	0·2046	0·2284	0·2475	0·24922	0·28081	0·32996

E. Grüneisen found 0·2068 between −190° and 17°, and 0·2485 between 17° and 100° ; T. W. Richards and F. G. Jackson gave 0·208 between −188° and −20°, and for the **atomic heat** between −188° and 20°, they gave 5·06, and between 20° and 100°, 6·0. P. Nordmeyer and A. L. Bernoulli, etc., have also made determinations of the sp. ht. of magnesium at different temp. R. J. Brunner gave for magnesium at $\theta°$:

	−273°	−200°	−100°	0°	100°	200°	400°	500°
Sp. ht. . . .	0·1104	0·1622	0·2101	0·2386	0·2557	0·2691	0·3171	0·3673
At. ht. . . .	2·689	3·949	5·116	5·810	6·226	6·554	7·721	8·944

P. Schübel obtained 0·2475 at 100° ; 0·2526 at 197° ; 0·2605 at 304° ; 0·2631 at 400° ; and 0·2680 at 500°. E. D. Eastman and W. H. Rodebush also determined values for C_p and C_v at temp. ranging from 74·9° K. to 288·5° K. W. Nernst and F. Schwers found C_p=4·558 at 93·8° K., and 0·335 at 27·2° K. G. N. Lewis and co-workers, and E. D. Eastman found the atomic **entropy** at 25° and one atm. to be 8·3 cals. per degree. L. Lorenz found the **thermal conductivity** in cals. per cm. per sec. per degree difference of temp. to be 0·3760 at 0°, and 0·3760 at 100°. The **heat diffusivity** of magnesium is 0·883 computed from $h^2=k/CD$, where k is the conductivity, C, the sp. ht., and D, the sp. gr.

P. Drude [3] estimated the **index of refraction** of magnesium to be 0·37 for λ=0·589μ ; the corresponding **absorption index** was 4·42 ; and the percentage **reflecting power,** 93. W. W. Coblentz found the reflecting power of magnesium for light of wave length λ to be :

Wave length, λ .	0·5	0·6	0·8	1·0	2·0	4·0	7·0μ
Reflecting power .	72	73	74	74	77	84	91 per cent.

Plane polarized light reflected from a polished surface is generally elliptically polarized, and for a certain angle, the **angle of principal incidence,** ϕ, 77° 57′, the change is 90°, and if the plane polarized incident beam has a certain azimuth, **angle of principal azimuth,** ψ, 42° 42′, circular polarized light results. The **refraction equivalent** of magnesium in salts for rays of infinite wave length is 6·51, according to J. Kanonnikoff, and 6·7, according to J. H. Gladstone, when calculated by J. H. Gladstone and T. P. Dale's formula. W. J. Pope gave 8·81 for the eq. refraction of magnesium for the D-ray. S. Procopiu found that the birefringence of toluene is positive, but negative when finely divided magnesium is suspended therein. Similarly with benzene, etc.

R. Bunsen and H. E. Roscoe measured the **actinic value of the magnesium light** compared with that of the sun. The visible brightness of the sun's disc, as measured by the eye, is 524·7 times as great as that of burning magnesium when the sun's zenith distance is 67° 22′, while at the same zenith distance, the sun's chemical brightness is only 36·6 times as great. This emphasizes the value of the magnesium light as a source of chemically active rays. The intensity of the magnesium flame was also studied by L. Troost, J. M. Eder, and H. Vogel. The combustion of 0·1 grm. of the metal can theoretically furnish as much light as 74 stearin candles burning for 10 hrs. A magnesium wire, 0·297 mm. diameter, burning in air gives as much light as 74 stearin candles each weighing 100 grms. K. Heumann found that the magnesium flame in sunlight gives an intense shadow, and he assumed that the flame of magnesium is non-luminous, and that the luminosity of the burning metal is really due to the magnesium oxide suspended in the flame. A. R. von Schrötter also studied the nature of the magnesium light E. L. Nichols found that the efficiency of the **light-energy** of burning magnesium is 10 per cent. of the heat

of combustion, a value unapproached among the known transformations of energy used in the production of light.

According to T. Tommasina, magnesium becomes **fluorescent** when used as electrode in an inductorium, under water or alcohol, but not under vaseline or petroleum. W. Ramsay and J. F. Spencer[4] gave the order Al, Mg, Zn, Sn, Cd, Pb, . . . for the **photoelectric effect** with polished metal surfaces and a mercury vapour lamp with uviol glass; K. Herrmann gave Al, Zn, Mg, Sn, Bi, Cd, Pb, . . . with a carbon arc-lamp; R. A. Millikan and G. Winchester gave Al, Mg, Sb, Zn, Pb, . . .; the latter also gave 0·839 volt at 26° for the positive potential of magnesium in vacuo in ultra-violet light. T. C. Sutton, and A. E. Henning and W. H. Kadesch have also studied the phenomenon with magnesium. A. Nodon found a sheet of magnesium is opaque to the penetrating solar photogenic radiations, but a metal of high valency is not. The absorption coefficient, μ, for the **β-rays** is approximately proportional to the sp. gr. D, and for magnesium $\mu/D=5{\cdot}1$. W. Duane, and E. Hjalmar measured the absorption frequencies for the X-rays.

W. A. Miller[5] first examined the spectrum of magnesium as obtained by introducing the chloride in the alcohol flame. The **spectrum** of burning magnesium has three green lines—5184, 5173, and 5167—and is very rich in the chemically active rays at the violet end of the spectrum. The light causes the detonation of a mixture of hydrogen and chlorine; it colours silver chloride dark blue in a few seconds, and, according to A. Schrötter, and H. Lallemand, it causes numerous bodies to phosphoresce. Magnesium salts do not impart any colour to the flame. The spark spectrum of the chloride shows an intense line, 5184; and a strong double line, 5173–5167, at 76 on the scale of Fig. 2. The double line is really a triplet, and

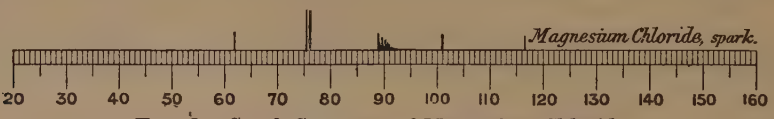

Fig. 2.—Spark Spectrum of Magnesium Chloride.

it coincides with the dark "little *b*" line of the solar spectrum. There is a shaded band beginning at 83·8, and fading away towards the blue end of the spectrum; and a feeble line at 4705, and another indigo line at 4481. The blue band in the spectrum is supposed to be due to magnesium oxide, and it is very bright in the spectrum of burning magnesium; the other lines are due to the metal itself. C. Cappel claims that 2×10^{-6} mgrms. of magnesium can be detected by the spark spectra; and W. N. Hartley found 10^{-7} mgrms. by photographing the ultra-violet spark spectrum. G. Kirchhoff identified the three green lines in the spectrum of magnesium with the "little *b*" lines in the solar spectrum. E. Carter examined the vacuum spark spectrum. R. W. Wood and D. V. Guthrie, F. Exner and E. Haschek, G. D. Liveing and J. Dewar, J. C. McLennan and co-workers, A. Cornu, and W. A. Miller examined the **ultra-violet spectrum.** J. Meunier found in the ultra-violet region the band composed of the rays λ=3810, 3829, 3833, 3838, 3851, 3858, 3861, and another band consisting of the rays λ=3885, 3912, 3940, 3960, 3980. Nine other rays between λ=3700 and 3780 have been noticed and their wave lengths approximately determined. Of the salts of magnesium, the chloride, oxychloride, sulphate, nitrate, oxide, and carbonate gave the above spectrum. The pyrophosphate is not, apparently, reduced under these conditions and does not give the above spectrum, since incandescence phenomena, corresponding with the continuous spectrum, are produced. F. Paschen, H. Lehmann, and H. Becquerel examined the **ultra-violet spectrum** of magnesium; W. W. Coblentz, R. A. Millikan and H. Becquerel, the **infra-red spectrum;** J. Stark and G. von Wendt, the effect of the **canal rays;** F. L. Mohler and P. D. Foote studied the **X-ray spectrum** of magnesium; W. Miller and T. Royds investigated the **Zeeman effect.** T. Takamine and N. Kokubu studied the effect of an *electric field* on the spectrum of magnesium. C. Olmsted studied the spectra of *magnesium fluoride, chloride, bromide, and iodide;* W. N. Hartley,

and E. E. Brooks, the spectrum of *magnesium nitride*; W. N. Hartley, *magnesium sulphate*; G. D. Liveing and J. Dewar, G. L. Ciamician, J. N. Lockyer, W. N. Hartley and H. Ramage, E. E. Brooks, A. Fowler and H. Payn, R. A. Porter, and O. H. Basquin, *magnesium hydride*; E. E. Brooks, W. N. Hartley and H. Ramage, J. M. Eder, E. Demarçay, L. de Boisbaudran, A. Gouy, W. M. Watts, H. Crew and O. H. Basquin, C. Olmsted, etc., the spectrum of *magnesium oxide*. G. A. Hemsalech showed that the spectral lines excited thermo-electrically and chemically are of the same type. E. Gehrcke and L. C. Glaser examined the *band spectrum* of magnesium. A. de Gramont and G. A. Hemsalech studied the effect of electric charge on the spectral lines of magnesium.

The spectra of magnesium, zinc, and cadmium are characterized by the presence of triplets repeated over and over again; the triplets are close in magnesium, wider in zinc, and still wider in cadmium. H. Kayser and C. Runge arrange the triplets of magnesium in two series which they believe to be subordinate series, and represent the oscillation frequencies by the formulæ:

FIRST SERIES.	SECOND SERIES.
$10^8\lambda^{-1}=39796{\cdot}10-130398n^{-2}-1432090n^{-4}$	$10^8\lambda^{-1}=39836{\cdot}74-125471n^{-2}-518781n^{-4}$
$10^8\lambda^{-1}=39836{\cdot}79-130398n^{-2}-1432090n^{-4}$	$10^8\lambda^{-1}=39877{\cdot}95-125471n^{-2}-518781n^{-4}$
$10^8\lambda^{-1}=39857{\cdot}00-130398n^{-2}-1432090n^{-4}$	$10^8\lambda^{-1}=39897{\cdot}91-125471n^{-2}-518781n^{-4}$

which agree with 39 lines in the arc-spectrum of magnesium, with very small differences except in the red, when the difference between the observed and calculated

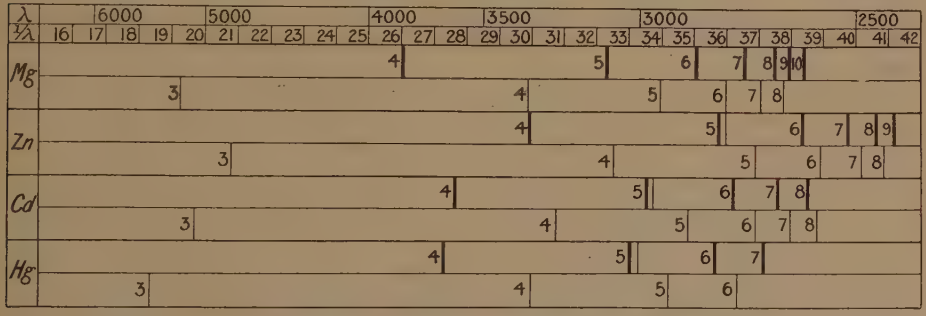

FIG. 3.—Series in Spectra of Magnesium, Zinc, Cadmium, and Mercury.

values is about one per cent. The coeff. of n^{-2} and n^{-4} in each series are the same, meaning that the spacing of the lines in the successive triplets are the same within the limits of experimental error. The arrangement of the lines in the series in the spectra of magnesium, zinc, cadmium, and mercury is shown in Fig. 3, the numbers of the lines represent the values assigned to n in the above formulæ. This subject has been discussed by A. Fowler. J. C. McLennan found that the vapour of magnesium gives a single line spectrum $\lambda=2852{\cdot}22$, when the heated vapours are bombarded by electrons whose energy is acquired by an arcing potential of 8·2 volts with Wehnelt's cathode and positive terminal. The **ionization potential** of magnesium vapour calculated by J. C. McLennan is 4·28 volts; M. N. Saha gave 7·65 volts or $1{\cdot}76\times10^5$ cals.; F. L. Mohler and co-workers, 8·0 volts; and J. C. McLennan and J. F. T. Young, 7·65 volts; K. T. Compton gave 3·63–4·28 for the minimum ionization potential. F. L. Mohler and co-workers gave 2·65–4·42 volts for the **resonance potential**. E. Rutherford and J. Chadwick obtained little, if any, evidence of the emission of long-range particles detached by scintillations on a zinc sulphide screen when **α-particles** pass through magnesium; and H. R. von Traubenberg found the range of the α-particles in magnesium to be $57{\cdot}8\times10^{-4}$ cms. M. N. Saha estimated the **temperature of complete ionization** to be 24,000° K., **luminescence** of the vapour to begin at 7500° K., and the temp. of maximum luminescence to be 11,000° K. B. E. Moore studied the excitation stages in the arc spectrum of magnesium.

According to A. Matthiessen,[6] the **electrical conductivity** of magnesium is a little less than that of zinc. L. Lorenz gave $24{\cdot}47\times10^{-5}$ for the electrical conductivity at 0°, and $17{\cdot}5\times10^{-5}$ at 100°; J. R. Benoit gave 24×10^{-4} for the cold hammered metal at 0°; and H. Ihle, $20{\cdot}8\times10^{-4}$ at 19°. J. Dewar and J. A. Fleming, and H. Dickson gave for zinc-free magnesium at −183°, $99{\cdot}9\times10^{-4}$ mhos; at −78°, $33{\cdot}7\times10^{-4}$; at 0°, 23×10^{-4}; at 98·5°, $16{\cdot}7\times10^{-4}$; and at 142·2°, $13{\cdot}5\times10^{-4}$; in addition, G. Niccolai gave:

	−189°	−100°	0°	100°	400°
Conductivity .	$78{\cdot}4\times10^{-4}$	$37{\cdot}8\times10^{-4}$	$23{\cdot}2\times10^{-4}$	$16{\cdot}9\times10^{-4}$	$8{\cdot}41\times10^{-4}$

E. F. Northrup measured the electrical resistance of magnesium between 20° and 100°. L. Cailletet and E. Bouty, and P. W. Bridgman gave 0·00390 for the *temperature coefficient* of the electrical conductivity between −88·31° and 0°. J. Dewar and J. A. Fleming gave 0·00381 between 0° and 100°. P. W. Bridgman found $-0{\cdot}0_5555$ for the *pressure coefficient* of magnesium at 0°; and later, with a purer sample, he obtained $0{\cdot}0_5390$ between 0 and 12,000 kgrms. per sq. cm. press. The results are:

		0°	50°	100°
Electrical resistance .		1·0000	1·1975	1·3900
Press. coeff.	0 kgrm.	$-0{\cdot}0_5477$	$-0{\cdot}0_5462$	$-0{\cdot}0_5473$
	12×10^3 kgrms.	$-0{\cdot}0_5311$	$-0{\cdot}0_5348$	$-0{\cdot}0_5341$
	Average .	$-0{\cdot}0_54080$	$-0{\cdot}0_54065$	$-0{\cdot}0_54018$

It was further found that the purer the sample, the smaller the temp. coeff. This is not usual, although L. Holborn found it to be the case with aluminium. W. P. Davey gave 0·90 A. for the **ionic radius** of the magnesium ion in magnesium oxide.

Magnesium is electrically negative against the metals of the alkalies and alkaline earths. According to J. F. Daniell and F. Exner, the **electromotive force** of an element Mg|Br is 2·36 volts, and of an element Mg|I, 1·57 volts. W. R. Mott measured the potential difference between magnesium and some of its salt soln., at 20° against a normal electrode −0·5 volt, and found with Mg—NaCl (2 mols per litre), +1·163 volts; Mg—NaOH (one mol per litre), +1·111 volts; Mg—KOH (one mol per litre), +1·140 volts; Mg—KOH (0·1 mol per litre), +1·105 volts; and Mg—$MgSO_4$ (one mol per litre), +1·366 volt. According to C. M. van Deventer, magnesium, when immersed in a mixture of alcohol and water, may become cathodic to zinc, immersed in dil. sulphuric acid. The change of potential is due to the formation of a layer of insoluble badly conducting salt on the magnesium. N. R. Dhar studied the e.m.f. of magnesium against aq. soln. of magnesium and potassium chlorides, and gave 0·81 volt for the potential against water. The e.m.f. in water or a neutral electrolyte is less than in a soln. of its own salt. W. Kistiakowsky measured the potential of cells of the type Mg|*N*-Mg-ions|*N*-H-ions|H_2 on Pt. The maximum potential of the **magnesium electrode** agrees with the assumption that the heat evolved by the reaction is $\frac{1}{2}Mg+H_2O=\frac{1}{2}Mg(OH)_2+\frac{1}{2}H_2+40{\cdot}28$ Cals.; and it is inferred that the potential of the magnesium electrode is fixed by the free energy of the reaction $\frac{1}{2}Mg+OH'-\ominus=\frac{1}{2}Mg(OH)_2$, just as the potential of the hydrogen electrode is fixed by the free energy of the reaction $H_2O+\ominus=\frac{1}{2}H_2+OH'$. The fact that the potential of the magnesium electrode is independent of the conc. of the Mg-ions, and that it reaches a maximum in reducing soln., and a minimum in oxidizing soln., is taken to support the hypothesis. J. Heyrovsky found the decomposition potential of magnesium to be −1·903 volts. L. Cambi found evidence of the **passivity of magnesium** and its amalgams during his measurements of the e.m.f. of this metal in pyridine soln. of magnesium chloride or iodide, but not when methyl alcohol was used as solvent.

The electric current generated by heating a junction of two different metals, or the same metal in two different conditions, is called a thermoelectric current, or the **Seebeck effect.** If the two junctions of a couple be initially at $T°$, and the temp. of one be raised by a small increment dT, when dE is the corresponding e.m.f., the ratio dE/dT is the thermoelectric power

of the two metals at $T°$. When an electric current flow passes in a closed circuit containing different metals, heat is absorbed at the junction which would have to be heated in order to give a thermoelectric current in the same direction as that given by the battery, and conversely for the other junction. The phenomenon is called the **Peltier effect**. Again, if a current passes in a closed circuit containing different metals with hot and cold junctions, there is an absorption or evolution of heat. Thus, heat is absorbed when a current flows from the cold to the hot junction in copper, and conversely; heat is evolved when a current flows from cold to hot in iron, and conversely. This phenomenon is called the **Thomson effect**. The Thomson effect with copper, silver, zinc, cadmium, and antimony is said to be positive; with iron, bismuth, cobalt, nickel, and platinum it is said to be negative; and with lead, the effect is neutral.

J. Dewar and J. A. Fleming's value for the **thermoelectric force,** or the **Seebeck effect,** of magnesium at 100° is 0·42 millivolt; K. Noll's 0·40 millivolt; and E. Wagner's, 0·43 millivolt; and the current goes to the platinum from the junction, at 0°. P. G. Tait represents the thermoelectric powers, E, of a circuit of magnesium and lead with one degree difference of temp. as $dE/d\theta=2{\cdot}22-0{\cdot}0094\theta$ microvolts, when θ represents the mean temp. of the two junctions; when θ is 20° and 50°, the respective thermoelectric powers are 2·03 and 1·75 microvolts; the neutral point is 236°, when $dE/d\theta$ is zero. P. W. Bridgman found the thermal effect, E, of magnesium against lead at atm. press. to be very small, $E=(-0{\cdot}095\theta+0{\cdot}00004\theta^2)\times10^{-6}$ volts; the Peltier effect, P, against lead is $P=(-0{\cdot}095+0{\cdot}00008\theta)(\theta+273)\times10^{-6}$ volts; and the Thomson effect, σ, against lead is $\sigma=0{\cdot}00008(\theta+273)\times10^{-6}$ volts per degree. The thermal e.m.f. of a couple composed of one branch of the uncompressed metal and the other compressed at p kgrms. per sq. cm., with the junctions at 0°, are in volts $\times10^6$,

p	10°	20°	40°	60°	80°	100°
2,000	−0·17	−0·33	−0·67	−1·00	−1·34	−1·67
6,000	−0·57	−1·04	−2·18	−3·43	−4·57	−5·71
12,000	−1·30	−2·59	−5·18	−7·78	−10·37	−12·96

The curves of e.m.f. at constant temp. against press. are concave upwards corresponding with an increasing proportional effect at higher press.; at constant press., the e.m.f. against temp. is linear. For the **Peltier effect** between the compressed and uncompressed metals, in joules per coulomb $\times10^6$, P. W. Bridgman found:

	0°	20°	40°	60°	80°	100°
p 2,000	−4·56	−4·91	−5·24	−5·56	−5·89	−6·23
p 6,000	−15·6	−16·7	−17·9	−19·0	−20·1	−21·1
p 12,000	−35·4	−38·0	−40·6	−43·2	−45·8	−48·4

The Peltier effect is thus negative and increases numerically with both temp. and press. The **Thomson effect** was found to be everywhere zero. According to M. E. Verdet, magnesium and its salts are diamagnetic; S. Meyer gave $+0{\cdot}57\times10^{-6}$ for the **magnetic susceptibility** of crystalline magnesium at 20°; and K. Honda gave $+0{\cdot}55\times10^{-6}$ at 18°. P. Pascal found the at. coeff. of magnetization to be -113×10^{-7} units. A. Günther-Schulze [7] studied the **electrolytic valve action** of magnesium in aq. salt soln.

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§ 5. The Chemical Properties of Magnesium

Magnesium is used for making illuminating powders for flash-light photography; and for star-shells for illumination in warfare; it is used as a deoxidizer in making bronzes, nickel-silver, and other alloys; it is used in conjunction with aluminium for making light alloys—*e.g.* magnalium; and it is used in dehydrating oils—*e.g.* aniline oil—etc. The compounds of magnesium are used medicinally; in making

cements; and magnesia is employed for making the so-called magnesite bricks for lining basic steel furnaces, and electric steel furnaces.

According to J. B. A. Dumas,[1] magnesium absorbs about two-thirds of its vol. of **hydrogen**, which is evolved in vacuo at a red heat. C. Winkler stated that hydrogen is not absorbed by hot magnesium, but a slow absorption does occur if the metal be mixed with magnesia, and heated to redness in a stream of hydrogen for 4 hrs., and he believed that 6·42 per cent. of the metal has been converted into **magnesium hydride**. No other chemical evidence of the existence of magnesium hydride has been adduced. According to A. Fowler, the dark grey deposit formed by the passage of the arc in hydrogen probably contains magnesium oxide, since, when dissolved in acids, it gives less hydrogen than would be furnished by an equal weight of magnesium; there is no chemical evidence of the formation of a hydride. O. H. Basquin noted that the spectrum, in hydrogen, with the rotating metallic arc with aluminium, copper, magnesium, silver, or sodium, has characteristic lines not found with the arc spectrum in air, and "in lieu of a better hypothesis," he assumed that the lines are due to the formation of metal hydrides. W. N. Hartley did not favour the hypothesis because, in the case of sodium, the dissociation at barometric press. is complete at 422°. G. D. Liveing and J. Dewar attributed the line at λ=5210, and the attendant series to "a mixture of magnesium and hydrogen rather than to a chemical compound, because this expresses the facts, and we have not yet obtained independent evidence of any chemical compound of these elements"; but in a later paper, they stated that "the lines just indicated are due to a combination of hydrogen and magnesium, and are not dependent solely upon the temp." A. Fowler likewise assumed that magnesium hydride is concerned in the production of the flutings in the spectrum of a mixture of hydrogen and magnesium, and that the combination appears to take place directly under the influence of the arc, especially at low press., or with some forms of the spark discharge, or by the combustion of the metal in an atm. containing hydrogen either free or in combination. E. E. Brooks suggested that the compound is in most experiments decomposed as quickly as it is formed, and A. Fowler added that "a perfectly definite conclusion does not at present seem to be possible."

A. A. B. Bussy,[2] and R. Bunsen found that magnesium does not change in dry **air**, but, in moist air, it is soon covered by a white film of magnesium hydroxide, and H. St. C. Deville and H. Caron found that in ordinary air it is attacked superficially. E. Sonstadt also stated that magnesium contaminated with nitrogen (nitride) is not stable in air. The metal inflames when heated just above its m.p. in air, and burns with an intense white dazzling flame, and a white cloud of magnesium oxide is formed. W. Muthmann and K. Kraft give 540° for the ignition temp. of magnesium in oxygen. According to F. J. Rogers, the temp. of the magnesium flame is 1335°. According to A. K. Christomanos, and W. French, when a cold solid is introduced into the magnesium flame, a black spot surrounded by a white halo of magnesium oxide is formed; according to A. K. Christomanos, and G. Baborovsky, the black deposit may be a suboxide; and A. K. Christomanos, J. W. Mallet, and J. Pinnow say that an appreciable quantity of magnesium nitride is formed in the *smothered combustion* of magnesium, *i.e.* the combustion of the metal in a quantity of air insufficient to burn all the metal. H. Kämmerer observed the formation of appreciable quantities of nitric oxide when magnesium burns in a cylinder filled with air; P. L. Aslanoglou noted the formation of ammonia in the oxidation of magnesium in moist air. According to S. Kappel, if air be passed over magnesium in contact with potassium hydroxide, nitrous acid, ozone, and hydrogen peroxide are formed; if the metal is in contact with aq. ammonia, magnesium nitride and suboxide are formed. In **oxygen**, magnesium burns quantitatively to the oxide. N. B. Pilling and R. E. Bedworth found that magnesium at 500° in oxygen produces a discontinuous film of oxide which offers no impedance to further oxidation. The oxidation is at the rate of about 0·00052 grm. per sq. cm. per hour, a value about one-third as great as that for calcium at the

same temp. O. Ohmann found magnesium-wool burns with explosive violence when ignited with a Bunsen's burner.

According to A. A. B. Bussy, cold, recently boiled **water** is without action on magnesium, while with boiling water, some hydrogen is developed: $Mg+2H_2O=Mg(OH)_2+H_2$. On the other hand, J. von Liebig stated that boiling water is without action on the metal. R. Bunsen observed that the metal he prepared slowly decomposed cold water. It is not clear if all these samples of metal were free from the alkali metals or the water free from carbon dioxide. D. Vitali found water free from carbon dioxide gives no hydrogen in contact with magnesium. According to C. F. Roberts and L. Brown, magnesium has no action on distilled water which has been freed from gases by boiling and afterwards cooled out of contact with air. It reacts, however, with undistilled water, with unboiled distilled water, or with water which has been boiled and afterwards charged with oxygen or carbon dioxide, varying amounts of hydrogen being liberated. H. T. Barnes and G. W. Scherer showed that some hydrogen peroxide is formed in the reaction. W. Hughes found that the reaction between magnesium and water is very slow at the ordinary temp., but is greatly accelerated in presence of neutral and alkaline salts, such as sodium chloride, sodium hydrocarbonate, sodium carbonate, and magnesium sulphate. Experiments with sodium chloride soln. at 25° have shown that the initial rate at which hydrogen is evolved depends on the concentration of the dissolved salt. The reaction velocity has a maximum value for a soln. containing 32 mols of water per mol of sodium chloride. This maximum cannot be satisfactorily interpreted in terms of the physical properties of sodium chloride soln., and is regarded as evidence in favour of the specific nature of the catalytic action of the electrolyte present. According to A. Ditte, magnesium decomposes water at a temp. exceeding 70°. Water vapour, at not particularly high temp., is decomposed by magnesium; and the phenomenon is used as a lecture experiment—*vide* A. Duboin, H. Leffmann, G. T. Moody, M. Rosenfeld, etc. According to F. Kessler, burning magnesium is not extinguished when plunged into steam.

According to C. Weltzien, and G. Giorgis, a soln. of **hydrogen peroxide** dissolves magnesium; if atm. carbon dioxide be not excluded, the soln. becomes alkaline, and furnishes on evaporation needle-like crystals of magnesium carbonate, soluble in water; while if carbon dioxide be excluded, the metal is dissolved much more slowly, the water becomes alkaline, and on evaporation gives a flocculent residue, not soluble in water. H. T. Barnes and G. W. Scherer showed that with magnesium and aluminium electrodes in contact with water containing dissolved air, the e.m.f. slowly rises to about one volt, although the metals are close together in the electrochemical series; this is due to the formation of hydrogen peroxide by the action of water containing dissolved air on aluminium. When free hydrogen peroxide is added to the aluminium compartment, the e.m.f. rises to about two volts, and then gradually falls as the hydrogen peroxide is decomposed.

H. Moissan [3] found that magnesium burns vigorously in **fluorine** (*avec beaucoup d'éclat*), forming the fluoride. In 1830, J. von Liebig found moist **chlorine** gas inflames magnesium; and in 1852, R. Bunsen said that the warm metal burns in chlorine, and J. A. Wanklyn and E. T. Chapman said that magnesium remains bright for a long time in cold chlorine. R. Cowper found that dry chlorine gas does not attack magnesium. H. Gautier and G. Charpy kept liquid chlorine for 15 months in contact with magnesium without any appreciable action. R. Bunsen said that warm magnesium does not burn so readily in **bromine** vapour as it does in chlorine; and H. Gautier and G. Charpy, and J. A. Wanklyn and E. T. Chapman found that dry liquid bromine could be kept for a year in contact with magnesium without any appreciable action; bromine water, on the other hand, gives a regular development of hydrogen, and an oxybromide is formed. R. Bunsen said that magnesium burns vigorously when heated in **iodine** vapour, and T. L. Phipson distilled iodine from magnesium without appreciable action. F. J. Faktor stated that a soln. of iodine colours magnesium green, and a film of the iodide is formed,

and J. A. Wanklyn and E. T. Chapman, that an ethereal or alcoholic soln. of iodine acts very slowly on magnesium when warmed. R. Bunsen noted in 1852 that magnesium is readily attacked by **hydrochloric acid**—*vide* action of acids on copper, and also on zinc. P. T. Austen noted that when burning magnesium is introduced into gaseous **hydrogen iodide,** it continues burning for a moment, and is then extinguished. A soln. of bleaching powder, sp. gr. 1·04, was shown by A. D. White to act slowly on magnesium with the evolution of hydrogen; with hypochlorous acid, hydrogen is rapidly evolved and magnesium hypochlorite is formed. According to W. S. Hendrixson, when magnesium reacts with **chloric acid,** about 95 per cent. is converted into chlorate, and the remainder is spent in the reduction of the acid. C. Kippenberger reduced soln. of the chlorates to chlorides by means of magnesium. According to A. Ditte, with a cold aq. soln. of **iodic acid** iodine is liberated, and hydrogen evolved; and a very dil. soln. of the acid is coloured yellow by the iodine. According to D. Vitali, a soln. of iodic acid is first coloured yellow by magnesium, and a brown precipitate is formed containing magnesium iodate, while the colourless soln. contains iodide and iodate.

According to K. Seubert and A. Schmidt, the **alkali chlorides** are reduced to the metals when heated with magnesium in an atm. of hydrogen, lithium chloride being reduced most readily; the **alkaline earth chlorides** are also reduced in a similar way, and the reduction is more readily effected the smaller the at. wt. of the metal. Most **metal chlorides**—*e.g.* the chlorides of copper, silver, gold, zinc, cadmium, mercury, aluminium, thallium, lead, tin, arsenic, antimony, bismuth, chromium, tungsten, molybdenum, uranium, manganese, iron, cobalt, nickel, and platinum—are also reduced when heated with magnesium. According to S. Möller, *chemiluminescence* occurs when an **alkyl halide** in ethereal soln. reacts with powdered magnesium.

According to J. von Liebig,[4] molten **sulphur** reacts with magnesium, and, according to R. Bunsen and J. Parkinson, the reaction is vigorous with the red-hot metal, and the metal burns vigorously in sulphur vapour, forming magnesium sulphide. A. Orlowsky found that the reaction between magnesium and sulphur or a soln. of sulphur in carbon disulphide is exceedingly slight at ordinary temp. According to T. L. Phipson, and F. G. Reichel, the sulphur can be volatilized by heat from an admixture with magnesium filings without reaction. According to W. Spring, a mixture of sulphur and finely divided magnesium forms a polysulphide when subjected to a press. of 6500 atm. L. Kessler found that burning magnesium continues burning in an atm. of **hydrogen sulphide,** and also in an atm. of **sulphur dioxide.** In the latter case J. Parkinson found that there is a separation of sulphur, and the formation of a residue which gives off red fumes when treated with nitric acid, and magnesium sulphate being formed. According to J. Uhl, the residue after the combustion in sulphur dioxide contains sulphate, sulphite, and sulphide. With sulphurous acid, P. Schweitzer obtained sulphite, thiosulphate, and trithionate; and M. Billy obtained magnesium tetrathionate with a soln. of sulphur dioxide in absolute alcohol. C. Brückner found that when **sulphur trioxide** vapour is passed over red-hot magnesium powder, magnesia, sulphur dioxide, and magnesium sulphide are formed. R. Bunsen stated that magnesium dissolves with difficulty in conc. **sulphuric acid,** and J. von Liebig observed the development of sulphur dioxide, and A. Ditte, hydrogen sulphide and sulphur. The rate of dissolution of magnesium in dil. acids has been investigated by N. Kajander, and he found that the wt. of metal dissolved in unit of time is, *cæteris paribus*, a simple function of the mol. wt. of the acid, of its conc., and of the nature (water, saline soln., etc.) of the medium in which the reaction is effected. **Heat** accelerates the reaction only because it diminishes the internal friction of the liquid. P. B. Ganguly and B. C. Banerji found that a rod of magnesium partly immersed in dil. acid is most attacked near the surface of the liquid. K. Seubert and A. Schmidt found **sulphur chloride,** S_2Cl_2, gives sulphur when heated with magnesium.

According to C. Brückner, when an **alkali sulphite** is heated with magnesium, alkali sulphide and sulphate are formed, while the **heavy metal sulphites,** *e.g.* zinc

sulphite, furnish sulphur dioxide, and the metal oxide, sulphide, and sulphate. When the **alkali sulphates** are calcined with magnesium in a stream of nitrogen, the alkali polysulphide, thiosulphate, and sulphur are formed, but no sulphur dioxide is evolved; while the **alkaline earth sulphates,** and the **sulphates of magnesium, zinc, aluminium, and nickel** give sulphur dioxide and oxide; **cupric sulphate** also gives metallic copper; and the **sulphates of manganese and iron** give the higher metal oxide, thiosulphate, and sulphide as well as sulphur dioxide and sulphur. Some sulphates react giving sparks when they are triturated with magnesium. The products of the reaction in the cold are not the same as with heat; thus **nickel sulphate** gives nickel sulphide and magnesium oxide in the cold, and nickel sulphide, sulphur dioxide, and sulphur when heated. According to F. J. Faktor, when magnesium is calcined with **sodium thiosulphate,** the sulphide and sulphate are formed; and when magnesium is heated with a soln. of sodium thiosulphate the reactions are symbolized: $Mg+2H_2O=Mg(OH)_2+H_2$; $Na_2S_2O_3+H_2=H_2S+Na_2SO_3$; $Mg(OH)_2+2H_2S=Mg(SH)_2+2H_2O$. H. Mouraour also studied the action of magnesium on soln. of sodium thiosulphate. According to M. G. Levi, E. Migliorini, and G. Ercolini, magnesium rapidly dissolves in a soln. of **potassium persulphate,** with the evolution of gas; and the turbulent action of an aq. soln. of **ammonium persulphate** on magnesium, furnishes ammonia gas, etc.

F. W. Newmann[5] studied the absorption of **nitrogen** by magnesium at the cathode of a vacuum tube. Magnesium is not attacked by nitrogen in the cold. H. Erdmann found liquid nitrogen extinguished the flame of burning magnesium. F. Briegleb and A. Geuther prepared magnesium nitride by heating the metal in a stream of nitrogen or **ammonia.** H. N. Warren added that there is very little action below a red heat, although the metal becomes less fusible and burns with violent decrepitations when ignited; at a dull red heat, the metal becomes yellow with a golden lustre; and at a full red heat it forms an orange-yellow powder of the nitride. According to T. L. Phipson, and G. A. Maack, aq. ammonia does not react with magnesium in the cold. Dry liquid ammonia, according to F. G. Cottrell, does act slowly on magnesium, forming a faint blue soln., which gradually decomposes into amide and hydrogen, in a manner analogous with the corresponding reaction between liquid ammonia and the alkali and alkaline earth metals. Liquid **acetylene** at ordinary temp. has no appreciable action on the metal. Electrical conductivity measurements show no signs of the formation of magnesium amminocarbide or amminoacetylide, but mixtures of liquid ammonia and acetylene readily act on magnesium, forming a crystalline compound, $MgC_2.C_2H_2.5NH_3$, and some ethylene and ethane. The product is stable below 2°, but at this temp. it loses the eq. of $1{\cdot}5NH_3$, and the residue is stable between 2° and 60°, when it loses ammonia and leaves behind a mixture of magnesium amide and nitride. According to C. A. L. de Bruyn, anhydrous **hydroxylamine** is without action on powdered magnesium. L. Kessler found that the flame of burning magnesium is not extinguished in **nitrous oxide** or in **nitric oxide;** and P. Sabatier and J. B. Senderens found that magnesium filings begin to react with **nitrogen peroxide** at a dull red heat. R. Weber found **nitrogen pentoxide** only exerts a slight action on the metal; and J. J. Sudborough, that **nitrosyl chloride** has no action on the metal either in the cold or at 100°. According to W. N. Hartley, aq. soln. of **nitrates** are reduced by magnesium to nitrites, and C. Kippenberger showed that with a dil. soln. of a nitrate, the first reduction product is a nitrite, then hydroxylamine, and finally ammonia. These primary reduction products can interact with one another to yield secondary products—nitrous and nitric oxides, nitrogen, etc. J. von Liebig stated that with cold **nitric acid,** nitric oxide is evolved, while C. Montemartini found that nitrous and nitric oxides, nitrogen, ammonia, and hydrogen are developed. The amount of ammonia produced in the reaction between magnesium and nitric acid increases with the concentration of the latter until 40 per cent. acid is reached, the quantity then decreases. Much hydrogen is formed; the mixture of this gas and nitric oxide liberated by 13 per cent. acid may be exploded by an electric spark.

J. J. Acworth and H. E. Armstrong obtained less nitric oxide and more nitrous oxide and nitrogen than is the case with cadmium or zinc. According to E. Divers, magnesium and nitric acid produce some hydroxylamine which is decomposed so rapidly as to escape detection unless some hydrochloric acid is also present. For some unknown reason sulphuric acid useful in the case of zinc is unsatisfactory with magnesium. According to P. T. Austen, magnesium burns with a white light in the vapour of nitric acid. According to W. Eidmann, many **nitrogenous substances,** when heated with magnesium, furnish magnesium nitride; and carbo-nitrogenous substances may give magnesium carbide as well.

J. Parkinson, P. T. Blunt, H. Schönn, and O. Emmerling obtained magnesium phosphide by heating magnesium with **phosphorus.** A. Stock and B. Hoffmann obtained magnesium phosphide by heating the metal with **phosphorus nitride,** P_3N_5; K. Seubert and A. Schmidt obtained phosphorus by the action of magnesium on **phosphorus trichloride;** and B. Reinitzer and H. Goldschmidt found that magnesium reacts with **phosphoryl chloride,** $POCl_3$, at ordinary temp., forming phosphorus trichloride, magnesium chloride, and phosphate, as well as a red substance which they think is an oxide of phosphorus; the reaction is very vigorous at 100°. H. Mouraour found magnesium slowly attacks soln. of **disodium hydrophosphate;** and A. Duboin found that a mixture of a mol of normal **calcium phosphate** with eight gram-atoms of magnesium reacts vigorously when heated in an atm. of hydrogen, some phosphine being formed. J. Parkinson heated to redness a mixture of magnesium filings and **arsenic** in a stream of hydrogen, and obtained a hard brown mass, which rapidly disintegrates on exposure to air. J. Parkinson prepared a similar product with **antimony** and magnesium. A. Stock and W. Doht obtained a

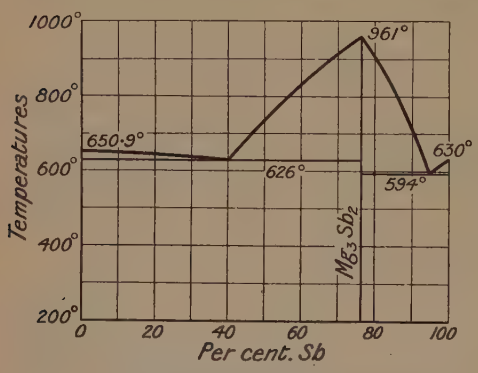

Fig. 4.—Freezing-point Curves of the Binary System Sb—Mg.

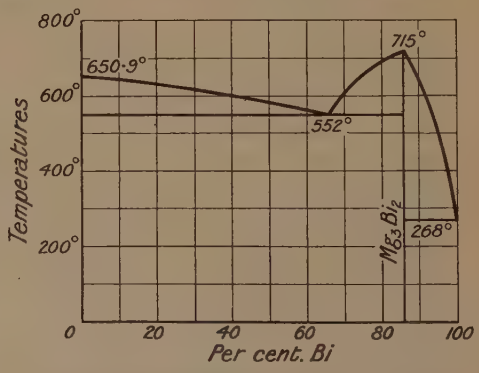

Fig. 5.—Freezing-point Curves of the Binary System Bi—Mg.

similar product. G. Grube obtained the f.p. curve shown in Fig. 4. There are two eutectics, with a maximum corresponding with **magnesium antimonide,** Mg_3Sb_2, melting at 961°. Magnesium readily alloys with **bismuth,** and G. Grube similarly obtained **magnesium bismuthide,** Mg_3Bi_2, melting at 715°, Fig. 5.

C. Winkler [6] observed that a superficial layer of magnesium carbide is formed when magnesium is heated with **carbon;** and J. Parkinson observed that some carbide is likewise formed when magnesium is heated in a stream of **benzene** vapour, although **methane** and **coal gas** have very little action. C. O. V. Engler and E. Kneis have studied the action of **petroleum** on magnesium, and found no appreciable solvent action after four months' exposure in air; the impure oil may exert a solvent action. K. Seubert and A. Schmidt found **carbon tetrachloride** forms carbon when heated with magnesium. According to L. Kessler, when a spiral of burning magnesium ribbon is immersed in **carbon monoxide,** combustion ceases; but if the metal be heated in a stream of the gas, vivid combustion occurs, and a grey coating of carbide is formed on the metal. J. Parkinson noted the separation

of carbon when magnesium is heated in an atm. of carbon monoxide. C. Winkler, and H. Cretier also made observations on the reduction of carbon monoxide by heated magnesium. V. Meyer seems to have regarded this gas as neutral at an incipient white heat. J. Parkinson, and L. Kessler noted that **carbon dioxide** is reduced to carbon by red-hot magnesium. C. Winkler showed that if magnesium be moderately heated in a stream of carbon dioxide, the metal is slowly converted into carbide, and some carbon monoxide is formed; on raising the temp. to a full red heat, the metal inflames, forming magnesia and carbon. These reactions are more readily observed if the powdered metal is employed. When a mixture of magnesium and calcium carbonate is heated in a current of hydrogen, a violent explosion occurs, and magnesium carbide is formed, but no calcium. K. Brunner found that when magnesium powder is scattered over a flat dish containing solid carbon dioxide and a small amount of burning magnesium is dropped into this, the metal continues to burn, forming a grey cake, which, on treatment with water and hydrochloric acid, leaves a residue of black, flocculent carbon. S. Kappel, M. Ballo, and G. Giorgis have studied the action of water saturated with carbon dioxide on magnesium—some hydrogen is developed but no magnesium carbonate is precipitated—water alone, under the same conditions, is without action on the metal. J. von Liebig found magnesium is attacked by cold dil. **acetic acid,** and R. Lohnstein found that the solvent action of dil. acetic acid on magnesium is inhibited if potassium dichromate is added in sufficient quantity to the soln. The magnesium loses its power of dissolving spontaneously in the soln., but, if it is made the anode of an electrolytic cell, it dissolves readily. The conc. of the dichromate required to produce the passive condition increases with the conc. of the acetic acid. If soln. still takes place, the rate is greatly diminished by the dichromate. The passive condition may be destroyed by the addition of an alkali or magnesium salt of a strong acid, the rate of soln. of the active magnesium increasing with the conc. of the added salt. R. Lohnstein suggested that the phenomena are of catalytic nature. According to A. Cavazzi, the vapour of **carbon disulphide** converts red-hot magnesium into the sulphide. According to A. Rossel, magnesium reacts with incandescence when heated in air with **calcium carbide:** $2CaC_2+6Mg+2N_2+5O_2=2CaO+2Mg_3N_2+4CO_2$. L. Kahlenberg and H. Schlundt found that magnesium is not attacked by anhydrous liquid **hydrogen cyanide,** nor by a soln. of sulphur trioxide; on the other hand, the metal is attacked by a soln. of hydrochloric acid or fuming sulphuric acid in that liquid. W. Eidmann found that when magnesium is heated with the **cyanides** of the alkalies or alkaline earths, the metal carbide and magnesium nitride are formed; the less stable cyanides—*e.g.* those of zinc, cadmium, nickel, cobalt, lead, and copper—react with incandescence, forming the metal magnesium nitride and carbon; and the unstable cyanides—*e.g.* those of gold and mercury—first decompose into the metal and **cyanogen,** which latter reacts explosively with magnesium. A. Brochet and J. Petit found that magnesium is vigorously attacked in the cold by a soln. of **potassium cyanide.**

According to C. Winkler, **silicon** reacts with magnesium with feeble incandescence when the two elements are heated together. G. Rauter found that magnesium exerts very little action on **silicon tetrachloride,** when heated for 67 hrs. to 390°–400°, although some silicon is formed; while K. Seubert and A. Schmidt say that much silicon is formed. T. L. Phipson and J. Parkinson found **silica** is reduced by magnesium when heated by the flame of a spirit lamp; C. Winkler found the reduction of the silica is attended by incandescence, and in the cooler parts of the containing vessel, bluish-grey magnesium silicide is formed, and in the hotter parts, brown amorphous silicon is formed. If an excess of silica be employed, no silicide is formed. **Silicates** were found by C. Winkler to be reduced like silica itself when heated with magnesium. J. von Liebig noted that **glass** on which magnesium has been burnt, and D. P. Smith that glass on which the metal has been fused, shows a black stain which is not removed by acids. V. Meyer found **porcelain** is strongly attacked by magnesium at an incipient white heat. According to J. Parkinson, and C. Winkler,

titanium dioxide is reduced by magnesium at a red heat, and the mass becomes incandescent—some *magnesium titanate*, but no *magnesium titanide* is formed. According to C. Winkler, **magnesium titanate,** $MgTiO_3$, is not reduced by magnesium. E. A. Schneider found **titanium nitride,** Ti_3N_4, reacts with magnesium like magnesium nitride, Mg_3N_2, reacts with titanium. T. L. Phipson found that **zirconium dioxide** is reduced by magnesium at the temp. of an alcohol flame; C. Winkler showed that the reaction is not complete, and if it takes place in an atm. of hydrogen some magnesium hydride is formed; no *magnesium zirconide* was observed. According to C. Winkler, **cerium dioxide** is reduced to the sesquioxide or the metal according to the proportion of *magnesium ceride;* **thorium dioxide** is incompletely reduced with feeble incandescence; **germanium dioxide** is very vigorously reduced to metal; likewise **stannic oxide** and **lead dioxide** are vigorously and violently reduced to the respective metals.

According to H. Moissan, when magnesium is heated with **boron** in a neutral atm., magnesium boride, Mg_3B_2, is formed; and with **boron sulphide,** boron and magnesium sulphide. K. Seubert and A. Schmidt say that boron is formed when magnesium is heated with **boron chloride.** T. L. Phipson, A. Geuther, H. N. Warren, A. Duboin, and L. Gattermann observed that **boron trioxide** is reduced by magnesium, forming boron, and C. Winkler obtained a mixture of boron and magnesium boride. H. Moissan has studied the reaction as a means of preparing boron. C. Winkler and L. Gattermann found fused **borax** is reduced like boron trioxide. J. Parkinson, and C. Winkler reduced **alumina** by magnesium; and the latter reduced **yttrium, lanthanum, gallium, indium, and thallium sesquioxides** in a similar way. J. Parkinson found **chromic oxide** is reduced by magnesium. W. R. Dunstan and J. R. Hill found that the immersion of the metal in one per cent. soln. of **potassium dichromate or chromate** furnishes **passive magnesium,** for the metal so treated and washed remained unchanged in distilled water for some hours under conditions where the untreated metal is oxidized all over. The passive metal is, however, also oxidized in about 24 hrs. A. Vyskocil also obtained passive magnesium. **Chromic acid** soln. act on magnesium tarnishing the surface. H. N. Warren found that **molybdenum oxide** reacts explosively with the element.

At a high temp. magnesium acts as a powerful reducing agent. H. N. Warren stated that magnesium does not reduce the alkali oxides and alkaline earths, but C. Winkler showed that this statement is wrong, for he found the **alkali hydroxides** and **alkali carbonates,** excepting cæsium carbonate, to be readily reduced by magnesium when a mixture of the two is heated in a sealed tube or in a stream of hydrogen. The reaction is very energetic with lithium and sodium carbonates. A. Geuther, and T. L. Phipson observed the ready reduction of sodium carbonate; the latter found the reaction occurred at the temp. of an alcohol flame. C. Winkler thought that cæsium carbonate was not reduced under these conditions, but the work of E. Graefe and M. Eckardt, N. N. Beketoff and A. Scherbatscheff, and of H. Erdmann and co-workers shows that cæsium hydroxide or carbonate is readily reduced. **Cuprous oxide** and **silver oxide** are violently reduced by magnesium; silver oxide and **gold oxide** are reduced by heat without the aid of magnesium. The **alkaline earth oxides** are readily reduced by magnesium; **beryllium, zinc, cadmium, and mercury oxides** are reduced explosively when heated with magnesium, but **magnesium oxide** is not changed. F. E. Weston and H. R. Ellis found that magnesium reduces **aluminium oxide** when the mixture is ignited with a fuse.

Magnesium acts as a reducing agent on soln. of salts of the metals. The available evidence is sometimes contradictory. Magnesium has been said to precipitate the element from soln. of salts of copper, silver, gold, zinc, cadmium, mercury, thallium, selenium, tellurium, arsenic, antimony, bismuth, tin, lead, manganese, iron, cobalt, nickel, platinum, and palladium; to precipitate the oxide from soln. of salts of chromium, and uranium; to reduce but not precipitate soln. of salts of molybdenum, tungsten, and vanadium. This subject had been investigated by G. A. Maack,[7]

T. L. Phipson, Z. Roussin, R. Böttger, C. Scheibler, etc. A. Vyskocil found that the ordinary equation for the speed of heterogeneous reactions cannot be applied to the reaction between magnesium and soln. of the ammonium salts, or of neutral metallic salts, since the metal first decomposes the water, and if the soln. is nearly neutral, the speed of the reaction depends to a great extent on the oxidizing or reducing power of the attacking soln. This view confirms V. Kistiakowsky's observations on the magnesium electrode. The anions of neutral salts in soln. act catalytically on the decomposition of water by magnesium. **Platinized magnesium** is also a powerful reducing agent; thus, according to M. Ballo, it reduces nitrobenzene in alcoholic soln. quantitatively to aniline. J. I. Michailenko and P. G. Mushinsky showed that the water of crystallization of certain salts is acted on by magnesium with the evolution of hydrogen.

According to F. Wöhler, aq. soln. of ammonium chloride or carbonate dissolve magnesium with the evolution of hydrogen; S. Kern, and D. Tommasi also found the attack is vigorous with soln. of ammonium chloride, and L. Santi, and D. Vitali stated that the double salt, $Mg(NH_4)_2Cl_4$, is formed; and H. Mouraour found soln. of various **ammonium salts**—carbonate, chloride, oxalate, and sulphide—act vigorously on magnesium, but no action was observed with soln. of ammonium fluoride. H. Mouraour attributed the specific action of soln. of the ammonium salts to their solvent action on magnesium hydroxide. D. Vitali found the action of a soln. of **hydroxylamine hydrochloride** to be analogous to that of ammonium chloride.

According to G. A. Maack, and T. L. Phipson, cold aq. soln. of the **alkali hydroxides** do not act on magnesium, and a similar observation was made by L. Kahlenberg with *N*-soln. of sodium and potassium hydroxides. The action of soln. of various **alkali salts** has been studied. H. Mouraour found a soln. of sodium carbonate is likewise attacked by magnesium. According to M. Ballo and G. Giorgis, aq. soln. of the alkali hydrocarbonates dissolve the metal with the evolution of hydrogen. According to S. Kern, when a soln. of sodium chloride is treated with magnesium, sodium hydroxide is formed with the slow development of hydrogen. D. Tommasi, however, states that in the case of potassium chloride soln. the action is catalytic, for the potassium chloride remains unchanged, and magnesium hydroxide is formed. As indicated above, W. Hughes found that the rate of evolution of hydrogen depends on the conc. of the soln., and there is a maximum with a soln. containing 32 mols of water per mol of sodium chloride; and the existence of this maximum is taken to correspond with a specific effect of the solute on the solvent. D. Tommasi and H. Mouraour also reported that aq. soln. of **salts of the alkaline earths** are feebly attacked by magnesium with the evolution of hydrogen. D. Tommasi found that with soln. of the alkali chlorides—of potassium, sodium, and lithium—magnesium furnishes hydrogen more rapidly than with water, and magnesium hydroxide is formed. H. Mouraour found soln. of sodium carbonate, acetate, and tetraborate react vigorously with magnesium, but soln. of sodium phosphate, nitrate, and thiosulphate, and potassium ferrocyanide react feebly. C. F. Roberts and L. Brown found that the hydrogen eq. of magnesium can be obtained with soln. of sodium, potassium, magnesium, barium, strontium, and calcium chlorides, but only very slowly with magnesium, and probably also potassium and sodium sulphates. The action is in general more rapid with the chlorides than with the sulphates; and the rate is dependent on the conc. of the soln., although no proportionality was observed. Fig. 6 illustrates the vol. increment of hydrogen per hour, with soln. containing

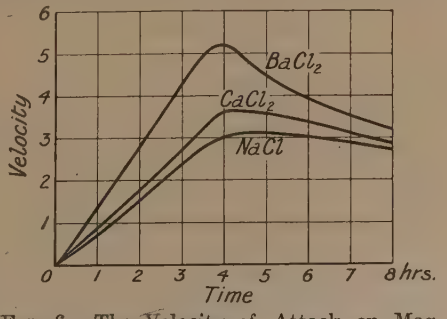

FIG. 6.—The Velocity of Attack on Magnesium by Solutions of Barium, Calcium, and Sodium Chlorides.

$\frac{1}{10}$-mol. per litre of the salts named—temp. 18°–19°. The maximum velocity is more quickly attained with the more conc. soln., but the reaction is completed in about the same time. With equi-mol. soln. of the chlorides the rapidity of the reaction is completed in about the order: magnesium (fastest), barium, strontium, calcium, sodium, and potassium (slowest). H. Mouraour found that soln. of potassium sodium tartrate (Seignette's salt) and sodium nitrite are slowly attacked by magnesium, while a soln. of sodium acetate is rapidly attacked.

D. Tommasi obtained cuprous chloride, cupric oxychloride, and hydrogen, but no copper, by the action of magnesium on soln. of **cupric chloride,** and K. Seubert and A. Schmidt found neutral soln. of cupric chloride gave a large proportion of cuprous oxide; ammoniacal soln. gave cuprous oxide and copper; and acidic soln. gave only copper; D. Tommasi obtained cuprous hydroxide, copper, basic copper sulphate, magnesium sulphate, and hydrogen as a result of the action of magnesium on a soln. of **cupric sulphate;** D. Vitali obtained copper, a blue basic copper salt, and hydrogen when magnesium acts on a soln. of a copper salt—*vide* the metallic precipitation of copper. The precipitation, according to E. G. Bryant, is never quantitative. According to D. Tommasi, when a soln. of auric chloride is treated with magnesium, gold, magnesium hydroxide and chloride, and hydrogen are formed; K. Seubert found auric chloride, and silver chloride in the presence of water are reduced to the metal. F. J. Faktor obtained analogous results with **salts of silver and gold,** and D. Vitali, and A. Villiers and F. Borg stated the metals are quantitatively precipitated by magnesium from these salts.

F. J. Faktor found that when **beryllium salts** are treated with magnesium, the corresponding hydroxide is formed. Magnesium liberates hydrogen from soln. of **magnesium salts.** D. Tommasi studied the reaction with magnesium chloride; G. Lemoine with aq. soln. of magnesium nitrate, chloride, sulphate, and acetate, when basic salts are precipitated, and the amount of hydrogen evolved is nearly proportional to the amount of magnesium dissolved. H. Mouraour, G. Platner, and C. F. Roberts and L. Brown, C. Kippenberger, etc., have also studied the reaction. L. Kahlenberg found that soln. of magnesium nitrate when treated with magnesium yield nitrite and finally ammonia, which accounts for the small amount of hydrogen liberated by this salt as compared with other salts of magnesium. From soln. of magnesium acetate and iodide, magnesium also evolves hydrogen rapidly. A magnesium sulphate soln. was treated with a large excess of finely divided magnesium, but no reduction of the salt to sulphite took place. He also studied soln. of magnesium chloride in glycerol, and in alcohol. S. Kern obtained zinc hydroxide by treating soln. of zinc salts with magnesium. K. Seubert and A. Schmidt found that a soln. of zinc chloride or cadmium chloride, with magnesium, gives the metal and hydroxide with neutral and ammoniacal soln.; and the metal with acid soln.; while D. Tommasi found that a soln. of cadmium chloride furnishes cadmium, cadmium oxychloride, hydrogen, and magnesium chloride; F. J. Faktor also found **zinc and cadmium salts** give the corresponding hydroxides. With a soln. of zinc sulphate, D. Tommasi obtained zinc hydroxide, zinc, basic zinc sulphate, magnesium sulphate and hydrogen. According to H. N. Warren, zinc is precipitated by magnesium from soln. in acetic acid. According to D. Tommasi, **mercuric chloride** furnishes mercurous chloride, mercuric oxide, magnesium chloride and hydrogen. D. Vitali found hydrogen, mercuric and mercurous oxides, and mercuric oxychloride were formed with mercuric chloride soln. K. Seubert and A. Schmidt obtained with neutral and acid soln. of mercuric chloride, first mercuric chloride, and later, with neutral soln., mercury. S. Kern obtained with mercuric chloride a grey precipitate which rapidly reddened when heated. D. Vitali found that magnesium reacts with soln. of **mercuric cyanide,** forming hydrogen, mercury, hydrocyanic acid, and magnesium cyanide.

According to H. Mouraour, soln. of **sodium borate** (borax) and of **alum** are attacked by magnesium. According to S. Kern, aluminium salts are but slowly affected by magnesium. K. Seubert and A. Schmidt found that a neutral soln. of

aluminium chloride forms aluminium hydroxide, but there is no decomposition in acid soln.; and thallous chloride forms thallium. D. Vitali also obtained aluminium hydroxide from soln. of aluminium salts. F. J. Faktor also found that soln. of **thallium salts** furnish thallium, and a soln. of thallium alum gives thallic hydroxide.

D. Tommasi found that when a soln. of **lead chloride** is treated with magnesium, lead, lead oxychloride, magnesium oxychloride, and hydrogen are formed. S. Kern found that pulverulent lead is rapidly precipitated from an aq. soln. of lead nitrate by magnesium; K. Seubert and A. Schmidt found that soln. of lead chloride always give a precipitate of lead, while a neutral soln. of stannic chloride gives stannic hydroxide, and an acid soln., metallic tin. F. J. Faktor found soln. of **stannous and stannic salts** give the corresponding hydroxides.

D. Vitali found that when soln. of **arsenites** are treated with magnesium, arsenic, arsine, and hydrogen are produced; and with **arsenates,** a precipitate of magnesium arsenate is formed. F. J. Faktor found soln. of **antimony salts** give black flocculent antimony, stibine, and hydrogen. Similar results were obtained by K. Seubert and A. Schmidt with soln. of arsenious and antimonious chlorides; and acid soln. of **bismuth chloride** gave bismuth.

According to H. Mouraour, a soln. of **chrome alum** is attacked by magnesium. A soln. of **chromic chloride** was found by D. Tommasi to form chromic hydroxide, magnesium chloride and hydrogen, while K. Seubert and A. Schmidt obtained chromic hydroxide with neutral soln. of chromic chloride, and no decomposition with acid soln. According to F. J. Faktor, a soln. of **potassium dichromate** is converted magnesium to the chromate, while S. Kern stated that a soln. of potassium dichromate slowly forms magnesium chromate and potassium hydroxide. According to D. Tommasi, a soln. of **manganese sulphate** furnishes manganese hydroxide, magnesium sulphate, and hydrogen. K. Seubert and A. Schmidt found that a neutral soln. of **manganese chloride** gives manganous hydroxide, and no change occurs with an acid soln. S. Kern found manganous salts give brown manganosic oxide when treated with magnesium. According to H. N. Warren, manganese is precipitated from acetic acid soln. by magnesium.

According to D. Vitali, a soln. of **ferric salt** gives hydrogen, ferrosoferric oxide and metallic iron; a soln. of a **cobalt salt** first gives a blue basic salt, and then black metallic cobalt; and a soln. of a **nickel salt** is slowly coloured green owing to the formation of nickel hydroxide. According to D. Tommasi, a soln. of ferrous sulphate forms magnesium sulphate, hydrogen, and ferrous hydroxide when treated with magnesium; and a soln. of ferric chloride gives, without reduction, ferric hydroxide, ferric oxychloride, magnesium chloride, and hydrogen; he also found cobaltous chloride soln. give cobaltous hydroxide, magnesium chloride, and hydrogen. The action of magnesium on soln. of ferric sulphate has been studied by S. Sugden. S. Kern obtained ferric hydroxide from a soln. of ferric chloride. According to K. Seubert and A. Schmidt, neutral soln. of ferric chloride, cobaltous chloride, or nickelous chloride give the hydroxide, $M(OH)_2$; a similar result is obtained with cobaltous and nickelous chlorides in the presence of ammonia; and acid soln. of ferric and cobaltous chlorides give the metal, but acid soln. of nickelous chloride remain unchanged. According to H. N. Warren, iron, cobalt, and nickel are precipitated by magnesium from acetic acid soln. of the corresponding salts. F. J. Faktor, and H. Mouraour found soln. of **potassium ferricyanide** are reduced to ferrocyanide.

K. Seubert and A. Schmidt, D. Vitali, F. J. Faktor, and A. Villiers and F. Borg found soln. of **platinum tetrachloride** give platinum quantitatively when treated with magnesium; D. Tommasi reported the formation of magnesium hydroxide and hydrogen as well as platinum; S. Kern stated that hydrogen, platinum, and platinum dioxide are formed when a soln. of platinum tetrachloride is treated with magnesium; and with a soln. of a **palladium salt,** hydrogen, palladium monoxide, palladium, and palladium hydroxide are formed. A. W. Knapp showed that if magnesium powder be added to ten times its weight of water, and then to this

mixture is added such an amount of palladious chloride as contains $\frac{1}{100}$th part of the weight of magnesium, a brisk evolution of hydrogen occurs.

As a rule, magnesium precipitates the metals from neutral aq. soln. of the salts, in some cases hydroxides or basic salts are precipitated and there is a development of hydrogen, particularly in the presence of ammonium salts. G. Platner, and E. Divers explain the evolution of hydrogen by assuming that the hydrolysis of the salt furnishes an acid which directly attacks the magnesium—*vide* the action of magnesium on cupric salts in **3**. 21, 3. L. Kahlenberg gave a similar explanation for salts of the heavy metals, while H. Mouraour attributed the evolution of hydrogen to the secondary action of magnesium on water. A. Commaille, and R. M. Caven assume that a galvanic couple is formed by the metal precipitated on the magnesium, and this decomposes the water. G. Lemoine also attributed the action of magnesium on soln. of its own salts to hydrolysis, although, as L. Kahlenberg pointed out, the reaction of soln. of magnesium salts towards indicators may be perfectly neutral at the outset, but soon after the introduction of the magnesium, it becomes alkaline, and remains so. Consequently, he does not accept the free acid hypothesis with soln. of salts of the alkalies, alkaline earths, and magnesium ; but he rather assumes that the solvent water is bound to the solute in variable proportions and that if the chemical affinity between the magnesium and the soln. (regarded as a combination of solute and solvent) is sufficient to overcome the cohesion of the magnesium, the latter is attacked, hydrogen is evolved, and the other products may remain in soln. or be further decomposed into a hydroxide or basic salt. If no precipitate forms, the speed of the reaction is not diminished by a decrease in the surface of the magnesium.

Reactions of analytical interest.—Magnesium salts are colourless ; they do not give any distinctive flame reaction ; but they have a characteristic influence on the absorption spectrum of purpurin, hæmatoxylin, etc.[8] Soln. of magnesium salts do not give a precipitate with hydrochloric acid, nor with hydrogen sulphide. Neither **ammonium sulphide** nor **ammonium hydrosulphide** gives a precipitate with soln. of magnesium salts ; but if the ammonium sulphide contains free ammonia, a precipitate may be formed. Aq. **ammonia** produces a precipitate of magnesium hydroxide provided ammonium salts be absent ; about half the magnesium will be so precipitated, and the other half forms a soluble double salt, $(NH_4)_2MgCl_4$. According to F. Jackson,[9] the sensitiveness of the test with aq. ammonia in the absence of ammonium salts is 1 : 32000. P. Harting gave a sensitiveness of 1 : 4000. Aq. ammonia in the presence of ammonium salts gives no precipitate because of the formation of this double salt. Several other salts of the bivalent metals behave similarly—*e.g.* salts of zinc, manganese, iron, cobalt, and nickel ; the tervalent metals do not form these ammonium salts. In the absence of other ammonium salts, **ammonium carbonate** precipitates a basic carbonate, say, $Mg_4(CO_3)_3(OH)_2$, but usually only after boiling or long standing ; the composition of the precipitate, however, depends on the temp. and conc. of the soln. ; the carbonates of the alkalies behave similarly. According to F. Jackson, the sensitiveness of the test with ammonium carbonate is 1 : 200 ; and with sodium carbonate, 1 : 4000. Magnesium salts give no precipitate with **barium carbonate** at ordinary temp., but with long-continued boiling, magnesium is completely precipitated from soln. of the sulphate, and partially precipitated from a soln. of the chloride or nitrate. A soln. of **barium hydroxide** likewise precipitates magnesium almost quantitatively as hydroxide, provided ammonium salts be absent ; the hydroxides of the alkalies and alkaline earths behave similarly. No precipitation occurs with soln. of **hydrochloroplatinic acid,** with **sodium cobaltic nitrite,** with **hydrofluosilicic acid,** with **potassium chromate,** or with **sulphuric acid.** An **alkali phosphate** or **ammonium phosphate** is a characteristic reagent for magnesium ; it produces in soln. containing ammonium chloride, and even free ammonium hydroxide, a white crystalline precipitate of ammonium magnesium phosphate, $Mg(NH_4)PO_4$; very dil. soln. give a precipitate only after long standing. When the precipitate is calcined, it

forms magnesium pyrophosphate, $Mg_2P_2O_7$, in which form the magnesium can be weighed. According to F. Jackson, the sensitiveness of the test with disodium hydrophosphate is 1 : 128000 ; and, according to P. Harting, with ammonium phosphate 1 : 200000. The **alkali arsenates** behave like the phosphates and give a precipitate of ammonium magnesium arsenate, $Mg(NH_4)AsO_4.6H_2O$, which, on ignition forms magnesium pyroarsenate, $Mg_2As_2O_7$. If the soln. of magnesium salt be sufficiently dil., and a large proportion of ammonium chloride be present, no precipitation occurs with **ammonium oxalate.** A soln. of an **alkali acetate** gives no precipitate with magnesium salts. With **potassium ferrocyanide,** a cold dil. soln. of magnesium salts gives a white crystalline precipitate of potassium magnesium ferrocyanide after standing some time ; conc. soln. give a precipitate immediately ; if ammonium salts are present the triple salt ammonium potassium magnesium ferrocyanide is formed. According to F. G. Schlagdenhauffen,[10] the presence of 0·02 per cent. of magnesium sulphate or chloride can be detected in salts of the alkaline earths by a soln. of so much iodine in a 2 per cent. soln. of sodium or potassium hydroxide that the liquid has a golden-yellow colour. A red coloration or a brownish-red precipitate is formed, which, according to T. Rettie, has no definite composition, and is probably a mixture of iodine with magnesium hydroxide. Lithium salts do not give the reaction. According to L. Grimbert, the original soln. is unstable, and not so sensitive as the soln. made by adding a few c.c. of a 10 per cent. soln. of potassium iodide to the liquid under examination, and then adding one or two drops of a soln. of sodium hypochlorite (*eau de Javal*). J. Bellier recommends using a one per cent. soln. of potassium iodide sat. with iodine ; followed by a soln. of sodium hydroxide. According to L. Grimbert, the reaction is not so sensitive as the ammonium phosphate test, and the sensitiveness is 1 : 2000, while, according to J. Bellier, it is 1 : 20000.

The atomic weight of magnesium.—The hydrogen eq. of magnesium is about 12. J. J. Berzelius [11] assigned the formula MgO to the oxide. There was some discussion as to whether the formula was Mg_2O, MgO, MgO_2, or Mg_2O_3, with the corresponding at. wt. of the order of 12, 24, 48, or 36 respectively. The formula MgO was finally adopted because the corresponding at. wt. of magnesium is in harmony with J. H. van't Hoff's extension of Avogadro's rule ; with Dulong and Petit's rule ; with Mitscherlich's isomorphism rule ; and with its position between zinc and beryllium in Mendeléeff's periodic table. T. Thomson discussed the at. wt. of magnesium in 1821.

The ratio $MgSO_4 : BaSO_4$.—J. J. Berzelius made the first at. wt. determination of magnesium in 1812, by weighing the SO_3, in a given quantity of magnesium sulphate, as barium sulphate, and from the ratio $MgSO_4 : BaSO_4$ he computed an at. wt. 25·24, when oxygen 16 is taken as unit. J. L. Gay Lussac likewise used this method in 1819, and obtained 23·62 ; T. Scheerer, in 1846, 24·16, and in 1847, 24·20 ; V. A. Jacquelain, in 1851, 24·43 ; and A. Macdonnell, in 1852, 24·30.

The ratio $MgO : MgSO_4$.—J. J. Berzelius synthesized the sulphate, and from the ratio $MgO : MgSO_4$, obtained the at. wt. 24·20 ; and in 1826, 25·28 ; V. A. Jacquelain, in 1851, obtained 24·44 ; L. Svanberg and O. Nordenfeldt, in 1848, 24·71 ; J. F. Bahr, in 1852, 24·77 ; and J. C. G. de Marignac, in 1883, 24·372.

The ratio $MgSO_4 : MgO$.—V. A. Jacquelain, in 1851, calcined magnesium sulphate at a high temp. so as to convert it into the oxide, and from the ratio $MgSO_4 : MgO$, he computed an at. wt. 24·44 ; and J. C. G. de Marignac, in 1883, obtained 24·363. A. Macdonnell, in 1852, determined the ratio $MgSO_4.7H_2O : MgO$ from which he calculated the at. wt. 24·30.

The ratio $MgC_2O_4.2H_2O : MgO$, or $MgCO_3 : MgO$.—L. Svanberg and O. Nordenfeldt determined the ratio $MgC_2O_4.2H_2O : MgO$, by calcining the oxalate, and hence computed the at. wt. 24·72. R. F. Marchand and T. Scheerer, in 1850, likewise calcined the carbonate, and from the ratio $MgCO_3 : MgO$, calculated the at. wt. 24·04 ; and, in 1858, T. Scheerer obtained the value 24·01.

The ratio $MgCl_2 : 2Ag$, or $MgCl_2 : 2AgCl$.—In 1859, J. B. A. Dumas determined

the chlorine in a soln. of magnesium chloride by titration with a standard soln. of silver nitrate, and from the ratio $MgCl_2 : 2Ag$ computed the at. wt. 24·63; and T. W. Richards and H. G. Parker, in 1896, 24·362. The last-named also converted the chlorine of the magnesium chloride into silver chloride, and from the ratio $MgCl_2 : 2AgCl$, computed the at. wt. 24·373.

The ratio Mg : MgO.—W. M. Burton and L. D. Vorce, in 1890, converted magnesium, distilled in vacuo, into the nitrate, and then calcined the nitrate to convert it into the oxide; from the ratio so obtained, they computed the at. wt. 24·29. T. W. Richards and E. F. Rogers showed that important errors are likely to accrue owing to the occlusion of gases by magnesium oxide obtained by the ignition of salts, etc.

F. W. Clarke's calculations averaged 24·398, and B. Brauner's 24·36. The best representative value for the at. wt. of magnesium, according to the International Table, 1922, is 24·32. The **atomic number** is 12. A. J. Dempster claimed to have resolved magnesium vapour into **isotopes** of at. wt. respectively 24, 25, and 26, and in the proportions 6 : 1 : 1.

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§ 6. Magnesium Oxides and Hydroxide

In 1866, E. Beetz [1] prepared what he regarded as **magnesium suboxide** as a black deposit on the positive pole during the electrolysis of a soln. of magnesium sulphate or sodium chloride with magnesium electrodes—hydrogen is given off at both electrodes. If the current is arrested, the black substance forms white flecks in the electrolyte. According to G. Bobarovsky, the best yield is obtained by working with a high current density, at a low temp., and for a short period with soln. of sodium or potassium chloride, or magnesium chloride or sulphate, and particularly with an alcoholic soln. of potassium acetate—the black product is not obtained with alkali hydroxides or ammonium salt soln. F. C. Frary and H. C. Berman obtained the suboxide by electrolyzing magnesium and potassium chlorides in a graphite crucible. They added that it is not formed when oxygen is completely excluded from the electrolyte, by melting the mixture in a stream of hydrogen chloride, and continuing the passage of the gas during electrolysis. The addition of a little magnesium oxide to the electrolyte results in the formation of the suboxide.

G. Gore found that if magnesium in contact with platinum be dipped in a soln. of glacial acetic acid in absolute alcohol, the black deposit appears in a few hours, and grows thicker for a few days. The product is formed more slowly if magnesium in contact with platinum, palladium, iron, gold, or silver, be dipped in water in the presence of carbon dioxide, coal gas, carbon tetrachloride, or ethylene tetrachloride, but not with carbon disulphide. The black product is indeed formed if the foreign metal is not employed. S. Kappel obtained a black substance by passing a stream of air over magnesium in contact with ammonia. A. K. Christomanos also obtained a black deposit when a cold substance was introduced into the flame of burning magnesium.

The black deposit, said G. Bobarovsky, appears to be homogeneous under the microscope; and his analyses range from Mg_8O_5 to Mg_3O_2. G. Gore's product became white when heated. E. Beetz found that the suboxide decomposes water with the evolution of hydrogen, and the formation of a white precipitate—possibly magnesium hydroxide. According to F. C. Frary and H. C. Berman, the hydrogen is contaminated with 5 per cent. of nitrogen. E. Beetz found the black substance dissolves in acids with the evolution of hydrogen and the formation of a salt of ordinary bivalent magnesium. With aq. soln. of magnesium sulphate it forms basic magnesium sulphate, and it is soluble in aq. ammonium chloride. According to F. C. Frary and H. C. Berman, the black substance is without action on a soln. of anhydrous nickel chloride in absolute alcohol, whilst metallic magnesium rapidly precipitates nickel.

Magnesium oxide, MgO.—This oxide has also been called *magnesia, calcined magnesia, burnt magnesite, Talkerde, Bittererde, magnesia usta, magnesia calcinata, magnésie*, etc. It was discovered by A. Scacchi [2] at Monte Somma, Vesuvius, as a mineral, contaminated with more or less ferrous oxide, and called *periclase*—περὶ, about; κλάσις, fracture—in allusion to the cleavage. The mineral has also been found at Teulada (Sardinia), Leon (Spain), Predazzo (Tyrol), Nordmarken (Norway) and Langban (Sweden), Pulpit Rock (Tasmania), etc. Analyses have been reported by A. Damour, H. St. C. Deville, E. Heydecke, and others.

Magnesium oxide is a product of the oxidation of the metal. The oxide is also produced in the amorphous or crystalline form by the calcination of many of the salts of magnesium—*e.g.* the carbonate, sulphate, nitrate, etc. It is also made commercially for the manufacture of magnesia bricks by the calcination of magnesite

in kilns of various kinds—*vide* lime. W. C. Riddell and C. N. Schuette described a shift kiln for making caustic calcined magnesite. O. Schumann [3] also made it by the calcination of magnesium sulphide in a current of steam. Magnesium oxide is made by heating the chloride in a stream of moist air, or flue gas : $2MgCl_2+2H_2O=4HCl+2MgO$. This process has been studied by T. J. Pelouze, E. Solvay, C. Heinzerling and J. Schmidt, and by the Salzbergwerk Neu-Stassfurt; F. Konther made magnesia by heating magnesium chloride with calcium chloride when hydrogen chloride is formed, and the magnesium salt is transformed into the oxide, the remaining calcium chloride can be removed by leaching with water. H. P. Bassett converted the chloride into oxide by heating it with steam at about 480°–650°, and removing any chlorine compounds by washing.

The extraction of magnesia from sea-water has been discussed by T. Schlösing. Processes for the recovery of magnesia from magnesium chloride soln., kainite or carnallite lye, etc. have been patented by M. Schliephacke and H. Riemann, and Ramdohr, Blumenthal u. Co., Alkaliwerke Westeregeln, A. Feldmann, G. Rosenthal, R. Heinz, M. von Maltzan, A. Rümpler, A. Vogt, etc. A. Rümpler devised a process for the recovery of magnesia from beet sugar residues ; and C. J. Johanson, from mineral water residues. E. W. von Siemens and J. G. Halske patented a process for the recovery of magnesia from ferruginous magnesian minerals and silicates by calcination in a stream of sulphur dioxide and air, whereby the magnesium alone forms soluble sulphate. H. Holland, G. Mojon, and E. Priwoznik have discussed the extraction of magnesia from serpentine rocks.

G. d'Adelswärd patented a process for *the separation of magnesia from dolomite* involving the soln. of the carbonate in hydrochloric acid, and its subsequent precipitation with calcium hydroxide. J. B. M. P. Closson treated dolomite with an aq. soln. of magnesium chloride : $CaCl_2+MgCl_2+CaO.MgO=2CaCl_2+2MgO$. A small quantity of sugar or molasses greatly accelerates the decomposition. A compound of sugar and lime is produced, from which, by the action of magnesium chloride, calcium chloride, magnesia, and sugar are formed. The last again acts on more of the calcined dolomite, with the formation of the soluble sugar-lime, and so on. From the liquid finally obtained the sugar is removed as the insoluble tribasic sugar-lime compound by heating. C. Bernard and L. Ehrmann, and C. Scheibler proposed to extract lime from calcined dolomite by means of a soln. of sugar. The solubility of lime in this menstruum is high, and of magnesia, low. O. Henry slaked the calcined dolomite with water, and treated it with half the amount of pyroligneous acid or hydrochloric acid necessary to dissolve the whole. The lime was thus removed by "elective affinity," and the washed residue consisted of magnesia. T. Twynam also digested raw dolomite with pyroligneous acid, and found that the magnesia is first taken up, and then precipitated ; the calcium acetate soln. was decanted off. R. T. Stull found that by treating calcined dolomite with just sufficient sulphuric acid to combine with the contained lime, the magnesia content could be raised from 42 to 75 per cent. R. D. Pike said that the lime is reduced by agitating the calcined mineral in a closed vessel at 300°–600° in presence of a gas containing carbon dioxide and water vapour, and afterwards leaching with water.

According to G. Lemoine, by digesting dolomite with water charged with carbon dioxide, the magnesium carbonate dissolves more rapidly than the calcium carbonate. When the soln. is heated, the magnesium carbonate is precipitated, and the carbon dioxide which is evolved can be used over again ; G. Moressée also found that when calcined dolomite is powdered and suspended in water at 10°, through which carbon dioxide, at 5–6 atm. press., is passed, only the magnesium oxide is dissolved. The extraction of magnesite from dolomite by the fractional soln. with carbonic acid has been also investigated by F. Findeisen, and H. L. Pattinson. C. Kippenberger based a technical process for the decalcification of dolomite, and the preparation of magnesium carbonate from magnesite, bitter spar, and from kainite or carnallite liquors, upon the fact that alkali hydrocarbonate soln. do not dissolve ferric hydroxide or calcium carbonate. The mineral is powdered, dissolved in commercial hydrochloric acid, and the iron oxidized by warming gently with a

little nitric acid. The soln. is then precipitated with sodium carbonate in slight excess, the filtered precipitate shaken with a sufficiently strong soln. of alkali bicarbonate, and the soln. filtered after the lapse of 20 minutes, and set aside to crystallize. The mother liquor can be used again and again for the extraction.

A cheap process for the **decalcification of dolomite** would make the large deposits of dolomite available for the manufacture of magnesia firebricks. Processes involving the use of chemicals would probably make the cost rather too high for the recovered magnesia to compete with imported magnesite. Physical methods of separation based on (i) the difference in the sp. gr. of the lime and magnesia when calcined at a high temp. ; and (ii) the greater inertness of magnesia when the calcined mass is treated with water, do not give a good separation, although F. Findeisen recommended such a process in 1860, and H. Auzies and A. Segoffin have patented a process for the decalcification of dolomite by slaking and levigating calcined dolomite in a series of tanks. The magnesium hydroxide being lighter than the calcium hydroxide is carried further by the water. They said that the deposit in the tank is nearly pure magnesium hydroxide. The method was examined by J. W. Mellor. L. H. Duschak found the best calcination temp. is 900°–950°, and the water used for leaching should be free from carbon dioxide. If the dolomite has been calcined at a higher temp., and especially if " dead burnt," the extraction is very incomplete, and is not improved by fine grinding owing to the formation of an insoluble compound. R. T. Stull treated calcined dolomite with running water, and raised the magnesia content from 42 to 65 per cent. ; boiling the calcined dolomite with water, and running off the magnesium hydroxide by flotation raised the magnesia content from 42 to 65–75 per cent. H. G. Schurecht and D. Eyoub, and T. Simon also made some observations on this subject. W. Esch said that calcium oxide is leached from hot calcined dolomite by a soln. of calcium chloride ; and R. A. W. Black, by a soln. of carbon dioxide in water made alkaline with calcium hydrocarbonate.

J. J. Ebelmen obtained crystals of periclase by melting together lime and magnesium borate in a porcelain oven ; A. Daubrée, by decomposing magnesium chloride by lime at a red heat ; J. B. A. Dumas, by melting magnesium chloride ; H. Debray, by melting a mixture of magnesium and potassium sulphates ; H. St. C. Deville, by acting on red-hot magnesia with a slow current of hydrogen chloride ; A. Cossa, by strongly heating a mixture of magnesium sulphate and sodium chloride ; F. Fouqué and A. Michel-Levy, by acting on red-hot magnesium chloride with steam ; T. Hiortdahl, by melting magnesium chloride with silica and zirconia ; A de Schulten, by slowly cooling a molten mixture of potassium hydroxide and magnesia ; A. le Royer, A. Brun, and M. Collet, E. Sommerfeldt, F. Heussler, and H. Moissan, by heating magnesite in an electric arc furnace ; M. Houdard, by heating a mixture of magnesia with five times its weight of magnesium sulphide in a carbon crucible in an electric arc furnace ; and G. Brügelmann, by calcining the nitrate or hydroxide, not the carbonate, in a covered platinum crucible. J. Meunier prepared crystals by dissolving magnesia in hydrochloric acid, and after evaporating the soln. heating it until hydrogen chloride ceases to be evolved. When the product is heated to redness, the trace of hydrogen chloride which remains acts as a mineralizer, and " brilliant octahedrons and tetrahedrons of periclase deposit on the walls of the crucible and cover." R. Otto and J. H. Kloos found crystals of periclase in a kiln lined with magnesia blocks, and used for preparing chlorine from magnesium chloride. Periclase is also found in magnesia bricks which have been used as linings in high temp. furnaces.

H. Struve [4] found *magnesia usta* contained traces of ammonium nitrate, but no peroxide ; and H. Rose found that the product obtained from *magnesia alba* containing chlorine, still retained chlorine. In general magnesia prepared by the calcination of magnesite will retain the non-volatile impurities of the original. T. W. Richards and E. F. Rogers found that magnesium oxide prepared by calcina-

tion is far more prone to occlude gases during ignition than is the case with zinc, copper, cadmium, or nickel oxide. The amount varied from 0·5 to 1·9 c.c. of gas per 10 grms. of magnesium oxide, and the gas contained oxygen, nitrogen, and carbon dioxide—in one case respectively in the proportions 38·9, 58·9, and 2·2 per cent. According to J. Meunier, magnesia may be freed from calcium by igniting at a red heat and subsequently, after cooling, extracting with successive portions of a 10 per cent. soln. of sucrose, until the last extract does not give a turbidity with ammonium oxalate. The residue is then washed and dried. If further purification is desired, this material is dissolved in hydrochloric acid and the soln. evaporated to dryness. The residue is gradually heated to 800°–900° in a covered crucible, and magnesia is obtained in its crystalline form as periclase on the lid and sides of the crucible and on the surface of the amorphous magnesia in the crucible.

V. Kohlschütter and J. L. Tüscher [5] prepared **colloidal** magnesium oxide dispersed in a gaseous medium by making the metal one electrode of an electric arc, and oxidizing the vapour.

The physical properties of magnesium oxide.—V. Kohlschütter and J. L. Tüscher [6] obtained highly dispersed magnesia, without a solvent, by volatilizing the metal in an electric arc, and suddenly cooling the vapour by a current of air. The precipitation of the fume was effected by a high-tension electric field. The **crystals** of magnesium oxide, and periclase, belong to the cubic system. F. Rinne believes that there is a hexagonal modification of magnesium oxide. According to W. P. Davey and E. O. Hoffman, E. Schiebold, W. Gerlach and O. Pauli, A. W. Hull, R. W. G. Wyckoff and J. A. Hedvall, **X-radiograms** of crystals of magnesia exhibit a simple cubic lattice of the sodium chloride type with sides $4{\cdot}220 \pm 0{\cdot}02$ A. W. L. Bragg gives for the distance between the neighbouring atom centres as 2·11 A. J. A. Hedvall examined the X-ray spectra of magnesia prepared in different ways, and found no change in the structure to be produced by heating. According to A. Scacchi, the **specific gravity** of the mineral (natural crystals) is 3·75; A. Damour gave 3·674; A. Cossa, 3·642 at 12°; H. M. Goodwin and R. D. Mailey, 3·674 (20°); and A. Sjögren, 3·90. For the artificial crystals, J. J. Ebelmen gave 3·636; A. de Schulten, 3·566; E. Mallard, 3·50; R. Otto and J. H. Kloos, 3·555 to 3·571; M. Houdard, 3·579 at 0°; and E. Madelung and R. Fuchs, 3·466–3·476 (0°). The sp. gr. of the amorphous, white, voluminous powder was given by C. J. B. Karsten as 3·2; by J. B. Richter as 3·07; by R. Kirwan as 2·3; and by G. Brügelmann as 3·42; H. Beckurts found the sp. gr. of *magnesia usta levis*, obtained by calcining light magnesia alba, to be 2·74; that of *magnesia usta*, obtained by calcining heavy magnesium carbonate, to be 3·057; and that obtained from neutral magnesium carbonate, to be 3·69. The sp. gr. of amorphous magnesia depends upon the temp. of calcination, thus, A. Ditte found:

	350° (1 hr.)	440° (1 hr.)	*c.* 560° (1 hr.)	*c.* 1200° (12 hrs.)
Sp. gr. at 0°	3·1932	3·2014	3·2482	3·5699
Sp. gr. at 100°	3·0971	3·1263	3·1909	3·5131

H. Rose showed that the sp. gr. of amorphous magnesia was raised to 3·647 near that of the natural mineral after calcination in a porcelain oven—temp. near 1600°. H. Moissan further found that when magnesia is heated for 2 hrs. in a blast, with retort carbon as fuel, the sp. gr. at 20° was 3·577; when heated 2 hrs. in the electric arc, 3·587; and when heated in an electric crucible furnace, 3·654. H. M. Goodwin and R. D. Mailey gave 3·493 for the sp. gr. of fused magnesia at 20°. In some cases —G. Brügelmann, and K. Arndt—the sp. gr. of amorphous magnesia is stated to be greater than that of the crystalline or fused material—there is always a possibility that minute air blebs entangled in the fused material will spoil the observations. J. W. Mellor suggested the possibility of estimating the proportion of α-magnesia (low sp. gr. form) and β-magnesia (high sp. gr. form) in a given sample of burnt magnesite from the observed sp. gr., and the following data give an idea of the

rate of conversion from the presumably amorphous to the presumably crystalline variety. After a two hours' calcination between 1300° and 1350°,

Number of calcinations	1	2	3	4	5	6
Sp. gr.	3·16	3·32	3·46	3·54	3·59	3·60
Per cent. converted	—	26	54	70	78	80

V. Tadokoro found the sp. gr. of magnesia brick at different temp. to be

	20°	100°	200°	400°	600°	800°	1000°
Sp. gr.	2·295	2·291	2·285	2·266	2·247	2·231	2·213

The **hardness** of periclase is approximately 6 on Mohs' scale; the artificial crystals prepared by R. Otto and J. H. Kloos had a hardness between that of felspar and of quartz; and J. J. Ebelmen's crystals a hardness of 4. A. Reis and L. Zimmermann have discussed this subject. E. Madelung and R. Fuchs gave $0{\cdot}70–0{\cdot}80\times10^{-6}$ megabars per sq. cm. for the **compressibility** of artificial magnesia.

According to L. B. Guyton de Morveau,[7] magnesia fuses with difficulty in a fire fed with oxygen, and its surface has after cooling the appearance of a porcelain glaze. In 1802, R. Hare fused magnesia in the oxyhydrogen blowpipe flame, and in 1819 E. D. Clarke also found that magnesia is converted by the oxyhydrogen blowpipe flame into a kind of opaque glass, which scratches glass like the diamond. H. Davy also fused magnesia under the influence of a powerful voltaic current. H. Moissan fused magnesia in an electric arc furnace whose temp. was estimated to be 3000°. K. Arndt gives 2500° for the **melting point** of purified magnesia, and he said that magnesia cannot be melted in the oxyhydrogen flame unless it be contaminated with silica, iron oxide, etc. H. M. Goodwin and R. D. Mailey found that fragments of pre-fused oxide did not fuse or soften below 1890°; but above 1940°, the grains always fused together, and it was considered that 1910° may be taken as the approximate m.p. of the fused oxide—this temp. appears rather low, indicating that the oxide was not of a high degree of purity. W. Hempel found Veitsch magnesite fused at 1825°–1830°; and magnesia at 2250°; A. Lampen found that fused magnesia had a m.p. of 2000°; and a magnesia brick with a high percentage of iron at 1900° had its edges rounded, and was quite fused at 2000°. C. W. Kanolt gave $2800°\pm13°$ for the m.p. of magnesia; and O. Ruff, 2500°; and O. Ruff and P. Schmidt, 2800° in an atm. of nitrogen. H. Caron stated that magnesium oxide cannot be fused in a wind furnace at a white heat, but in the oxy-coal-gas flame, it melts, and partially volatilizes. E. Tiede and E. Birnbräuer could not melt magnesia, but said that volatilization begins at about 2000°. A. A. Read did not detect any change when magnesium oxide is heated to the m.p. of platinum. C. Despretz claimed that by the simultaneous action of a current from 185 Bunsen's cells, the burning glass, and a hydrogen flame, he was able to volatilize magnesia; and P. Lebeau has stated that magnesia boils vigorously when heated seven minutes by a current of 110 volts and 700 amps., and that the volatilization of the oxide is much faster in the presence of three or four times its weight of sugar charcoal—possibly owing to the intermediary formation of magnesium or magnesium carbide, for R. E. Slade has shown that magnesia can react with carbon at a temp. below the m.p. of the oxide. O. Ruff and P. Schmidt measured the **vapour pressure** of magnesia. According to O. Ruff and O. Goecke, the **sublimation temperature** at one atm. press. is about 2000°, and W. R. Mott estimated the **boiling point** to be 3600°; O. Ruff and P. Schmidt found 2800°–2850° in an atm. of an indifferent gas at 760 mm. E. Tiede and E. Birnbräuer found that magnesia dissociates readily at 1900° in a vacuum furnace producing a deposit of magnesium. E. W. Washburn computed the latent **heat of fusion** to be 30,000 cals. per mol, or 700 (±15 per cent.) cals. per gram.

H. V. Regnault found the **specific heat** of artificial magnesium oxide to be 0·24394 between 24° and 100°; and A. S. Russell found 0·1006 between −79·3° and −190·8°; 0·1933 between 0° and −79°; and 0·2385 between 1·4° and 48·6°. H. von Wartenberg and G. Witzel found the mol. ht. of magnesium oxide at 2780°

to be 11·6 cals. Observations were also made by W. Steger, and E. Heyn and co-workers. V. Tadokoro found the mean sp. ht. of a magnesia brick to be

	218°	303°	382°	480°	579°	687°	796°	894°
Sp. ht.	0·223	0·238	0·254	0·263	0·266	0·265	0·264	0·263

It is not clear if the decrease at the more elevated temp. is due to errors of experiment. Measurements of the sp. ht. at a low temp. were made by A. Magnus. H. M. Goodwin and R. D. Mailey found the linear **coefficient of thermal expansion** of fused magnesia at $\theta°$ between 120° and 270°, to be $\alpha=0{\cdot}00001140+0{\cdot}0000000092(\theta-120)$, a value not much greater than that for a quartz crystal cut parallel to its optical axis, and nearly equal to that of platinum. H. Fizeau found $\alpha=0{\cdot}00001043$ for the coeff. of expansion of periclase, and for the increase per degree rise of temp. $d\alpha/d\theta=0{\cdot}0000000267$. J. W. Mellor found $\alpha=0{\cdot}0000126$ for magnesite bricks between 15° and 1350°; H. J. Hodsman and J. W. Cobb obtained 0·00001274 for the coeff. of expansion of a magnesia brick between 15° and 1000°. B. Bogitch measured the expansion of magnesia bricks. V. Tadokoro found the mean coeff. of expansion of a magnesia brick to be

	20°	100°	200°	400°	600°	800°	1000°
Coeff. exp.	$0{\cdot}0_4000$	$0{\cdot}0_4063$	$0{\cdot}0_4131$	$0{\cdot}0_4142$	$0{\cdot}0_4126$	$0{\cdot}0_4125$	$0{\cdot}0_4128$

R. S. Hutton and J. R. Beard found that fused magnesia, powdered to pass a sieve with 600 meshes per sq. cm., had a **thermal conductivity** between 20° and 100° $k=0{\cdot}00047$ cal. per sq. cm. degree difference of temp., per second; against $k=0{\cdot}00029$ for lime; and $k=0{\cdot}00028$ for firebrick. He also found for a magnesia firebrick 0·00050; for calcined Greek magnesite, 0·00045; for calcined Styrian magnesite, 0·00034; and for lightly calcined magnesite, 0·00016. S. Wologdine found 0·0065 and 0·0055 for two magnesite bricks with respectively 41 and 35·1 per cent. porosity. B. Dudley obtained 0·0343 for the mean conductivity of a magnesia brick over the range from 445° to 830°. C. Dougill, H. J. Hodsman, and J. W. Cobb found the conductivity of a magnesite firebrick fell from $K=0{\cdot}017$ at 380° to 0·0132° at 700° to 0·00000091 at 1370°. V. Tadokoro found the thermal conductivity of a magnesia brick to be

	200°	300°	400°	500°	600°	700°	800°	900°
Conductivity $\times 10^3$	6·57	5·47	4·91	4·71	4·39	4·14	3·85	3·73

The **heat of formation** of magnesium oxide, according to J. Thomsen, is (Mg, O), 145·86 Cals.; H. von Wartenberg gave 143·9 Cals. According to the former, the heat of formation of magnesium hydroxide is (Mg, O, H_2O), 148·96 Cals., and (Mg, O_2,H_2), 217·32 Cals.; M. Berthelot gave respectively 148·8 and 217·8 Cals.; and for (MgO,H_2O), he gave 5·4 Cals. M. Berthelot also measured the heat of precipitation of magnesium hydroxide by adding a soln. of ammonia or sodium hydroxide to a soln. of a magnesium salt. J. Johnston gives for the free energy of the change hydroxide to oxide, 3600 cals. at 25°. According to A. Ditte, the **heat of the solution,** in sulphuric acid, of magnesia calcined at different temp. is very different:

Temp. calcination	350°	440°	*c.* 560°	*c.* 1200°
A. Ditte	832·8	920·8	961·7	1004·6 cals.
J. C. G. de Marignac	—	874	875	867 cals.

J. C. G. de Marignac examined what he called *l'influence prétendue* of calcination on the heat of soln., and his data are indicated along with those of A. Ditte.

E. Mallard[8] gave for the **index of refraction** of artificial crystals 1·7307 for Li-light, 1·7364 for Na-light, and 1·74133 for Tl-light; S. Sommerfeldt, 1·7298 for red light, 1·7350 for Na-light, and 1·7460 for blue light; A. Le Royer, A. Brun, and L. W. Collet gave 1·700 for red light, and 1·717 for green light. According to D. Brewster, H. Caron, and C. M. T. du Motay and C. R. M. de Maréchal, at a high temp. magnesia has a very high emissive power for light; the light is not very different from that of burning magnesium. F. Henning and W. Heuse studied the

reflecting power of magnesia. J. Drummond tried magnesia in place of lime for the lime-light, but found the intensity of its illumination to be less than half that of lime. H. E. Ives and co-workers studied the illuminating power and emissivity of mantles made of magnesia and heated by Bunsen's flame. The results compare favourably with those of thoria. W. Crookes, and H. Jackson found magnesia has a marked reddish **fluorescence** in the cathode rays, and L. de Boisbaudran found the fluorescence is a bright red if the magnesia has about one per cent. of chromium. P. Bary found that magnesia does not phosphoresce when exposed either to the **X-rays** or to **Becquerel's rays.** E. L. Nichols and D. T. Wilber found that magnesium oxide, like calcium oxide, exhibits **flame luminescence.** E. L. Nichols studied the brightness of the luminescence, and found that when heated to 1000° in the oxyhydrogen flame magnesia appears blue. W. W. Coblentz found a transparent region in the **ultra-red transmission spectrum** at 5μ, preceded and followed by almost complete opacity. The bands at $3{\cdot}3\mu$ and $3{\cdot}8\mu$ are virtually the same as those of calcite. The **ultra-red refection spectrum,** like that of calcite, has maxima at $6{\cdot}5\mu$ and $6{\cdot}8\mu$. E. L. Nichols found the **colour temperature** of incandescent magnesia is 5000°, while the actual temp. is not over 2000°.

According to F. Beijerinck,[9] periclase is a non-conductor of electricity at ordinary temp. H. M. Goodwin and R. D. Mailey found the specific **electrical conductivity** of small cylinders of fused magnesia at different temp. in mhos :

	700°	800°	900°	1000°	1050°	1100°	1150°	1500°
Sp. conductivity $\times 10^6$.	—	0·01	0·10	0·20	0·34	1·00	2·60	85·0

The results are plotted with those of porcelain in Fig. 7. Fused magnesia is thus a much better insulator than porcelain at temp. below 1100°, and above that temp., its conductivity exceeds that of porcelain. A. A. Sommerville found that a column of the oxide 1 cm. diam. and 10 cms. long has an electrical resistance of 10^7 ohms at 545°. According to F. Horton, the effect of temp. on the electrical resistance (ohms) and the electrical conductivity (mhos) of magnesia is

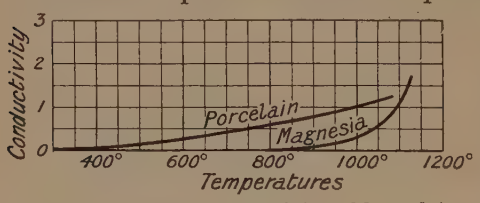

Fig. 7.—Specific Conductivity of Porcelain and Fused Magnesia.

	471°	630°	828°	1055°	1191°	1204°	1341°
Ohms .	35×10^6	8×10^5	88000	12450	4900	12900	29×10^4
Mhos .	$3{\cdot}69\times10^{-9}$	$1{\cdot}61\times10^{-7}$	$1{\cdot}46\times10^{-6}$	$1{\cdot}04\times10^{-5}$	$2{\cdot}63\times10^{-5}$	$1{\cdot}00\times10^{-5}$	$4{\cdot}45\times10^{-7}$

The electrical conductivity of magnesium oxide thus increases rapidly with the temp. up to 1200°–1250° and then decreases. If the temp. is kept constant above 1200°, the conductivity also decreases with the time. The phenomenon is probably due to a change of the oxide into a less conducting form of greater density. There is evidence of a slight electrolysis during the passage of the current. F. Kohlrausch and F. Rose found the specific conductivity of a sat. soln. of magnesium hydroxide at 18° to be 83×10^{-6} mhos; and F. Kohlrausch, 69×10^{-6} to 94×10^{-6} mhos. S. Glixelli measured the **electro-osmosis** of magnesium oxide. S. Meyer gives for the **magnetic susceptibility** $-0{\cdot}008\times10^{-6}$ units per mol, or $-0{\cdot}055\times10^{-6}$ units per grm. E. Thomson[10] has studied the orientation of fine particles of magnesium oxide in the magnetic field.

The chemical properties of magnesium oxide.—As indicated above, T. W. Richards and E. F. Rogers[11] found magnesium oxide prepared by the ignition of the nitrate or carbonate always contained occluded gas; the gas mainly consisting of oxygen and nitrogen, with a smaller proportion of carbon dioxide. J. A. Hedvall and N. von Zweigbergh have studied the action of **barium dioxide**

on magnesia. According to H. Davy, magnesia absorbs **chlorine** at a red heat, and forms magnesium chloride with the evolution of oxygen. V. H. Veley found that while dry **hydrogen chloride** has no action on magnesia at ordinary temp., a reaction occurs at about 40°. A. J. Balard stated that calcined magnesia is not decomposed by **bromine.** L. Meyer observed that when magnesia is heated in a stream of **carbon tetrachloride,** magnesium chloride, carbon dioxide and monoxide, and carbonyl chloride are formed. P. N. Raikow found **carbon dioxide** converts magnesium hydroxide into an acid carbonate. C. J. B. Karsten found that molten **sodium chloride** is not decomposed by magnesia. According to R. E. Hughes, dry **hydrogen sulphide** has not an appreciable action on dried magnesia between 15° and 40°, but in presence of moisture, the gas is absorbed; O. Schumann noted the formation of magnesium sulphide when hydrogen sulphide is passed over heated magnesia. E. Frémy observed that red-hot magnesia is converted into the sulphide by the vapour of **carbon disulphide.** K. Birnbaum and C. Wittich found that **sulphur dioxide** is absorbed by magnesia at 360°, but so slowly that three months are needed for the completion of the reaction. W. T. Smith and R. B. Parkhurst studied the absorption of sulphur dioxide by milk of magnesia. V. Lenher found magnesia dissolves in a soln. of **selenium oxychloride.** When magnesia is heated in a stream of **phosphorus pentachloride,** A. Daubrée noted the formation of crystals of normal magnesium phosphate. M. Berthelot and G. André found magnesia drives ammonia with difficulty from, even boiling, soln. of **ammonium salts**—thus ammonium magnesium phosphate is but very slowly decomposed when boiled with magnesium hydroxide suspended in water. The reduction of magnesia by **carbon** has been discussed in connection with the preparation of magnesium. E. Tiede and E. Birnbräuer said that magnesia is not reduced. O. P. Watts found magnesium oxide is more effectively reduced by certain **carbides** than by carbon alone. The carbides of iron, nickel, and chromium are very active, but those of copper and tin have scarcely any action on the reduction of magnesium oxide. W. G. Palmer found magnesia admixed with cupric oxide to act catalytically on the dehydrogenation of ethyl alcohol. **Siloxicon** and **carborundum** accelerate the reduction. H. Davy studied the action of the **alkali metals** on heated magnesia—*vide* magnesium. F. E. Weston and H. R. Ellis found that magnesia is reduced by **calcium,** but nitride is simultaneously formed. According to H. N. Morse and J. White, when a mixture of magnesia and **magnesium** is heated to redness in an evacuated tube, the magnesium oxide is transported to the cooler part of the tube. The phenomenon is not due to the volatility of the oxide, but is thought to be due to the free metal attracting the oxygen and causing a dissociation of the oxide, which reforms in the cooler part of the tube where the temp. is lower—*vide* zinc and cadmium oxides. C. Matignon argues that every system of liquid or solid bodies which is capable of giving rise to a system furnishing volatile substances, will undergo reaction in that sense at a convenient temp., and the reduction of magnesia by **aluminium**: $2Al+3MgO=3Mg+Al_2O_3$, is possible because magnesium is volatile at a comparatively low temp. F. E. Weston and H. R. Ellis stated that magnesia is not reduced by aluminium. R. Fink found that when magnesium hydroxide is added to soln. of manganese, iron, or nickel sulphate, basic salts of these metals are precipitated. S. Meunier found that molten potassium hydroxide dissolves half its weight of magnesia, and the molten mixture absorbs oxygen from the air. L. B. Guyton de Morveau heated mixtures of magnesia with **baryta** and with **lime,** but obtained no special results. E. S. Shepherd and co-workers found that the components of fused mixtures of lime and magnesia crystallize out side by side; they furnish a simple eutectic mixture with no evidence of combination; J. B. Ferguson and H. E. Merwin estimated a eutectic at about 2300° and about 32 per cent. MgO. According to J. J. Berzelius, when moistened with **cobalt nitrate,** and strongly ignited before the blowpipe, it takes a fine rose colour; and J. A. Hedvall noted the formation of mixed crystals of calcium and magnesium oxides.

P. Butini, H. Davy, etc., noted the inertness towards **water** of magnesia calcined at a high temp., and H. Rose stated that magnesia prepared by calcining *magnesia alba* does not become warm when mixed with water, while magnesia prepared by calcining trihydrated magnesium carbonate to 300°, becomes hot when mixed with water. The properties of magnesia calcined at high and at low temp. are therefore in marked contrast. As shown by A. Ditte, and W. C. Anderson,[12] the low temp. and low sp. gr. form readily absorbs gases, and moisture; it is readily and quickly dissolved by mineral acids; and it reacts quickly with water. The high temp., high sp. gr. form of magnesia is very resistant to these influences, and it remains practically unacted upon by water, even after the lapse of a considerable time. H. M. Goodwin and R. D. Mailey have stated that fused magnesium oxide possesses in a remarkable degree the ability to withstand the action of many **neutral salts** at high temp., and is therefore well adapted for use as vessels and apparatus for containing such salts when subjected to high temp. Silver, sodium, and potassium nitrates; sodium and potassium chlorides, bromides, and sulphates; zinc chloride; and barium nitrate showed no action on a polished sample of fused oxide when the latter was heated for an hour or more in the fused salt. Barium chloride had a very slight action; while **sodium carbonate, potassium carbonate, potassium hydroxide,** and **cryolite** attacked the fused oxide energetically. Dil. **nitric, hydrochloric, or sulphuric acid** slowly attacks the fused oxide in the cold; the conc. acids are less active than the dil. acids.

In addition to the manufacture from calcined magnesite of refractory firebricks for basic steel furnaces, the Königlichen Porzellan-manufaktur, Berlin, make various chemical apparatus—tubes, dishes, crucibles, etc.—from fused magnesia. According to K. Arndt, they can be heated in the blast flame without cracking, but, according to E. Wedekind, care is necessary on cooling. J. W. Mellor and F. Austin noted that fused magnesia does not crack like fused quartz does during its devitrification. E. Wedekind says fused magnesia undergoes no shrinkage or electrolysis when heated in the electric furnace at 1750°. In 1806, J. L. Proust mentioned the use of magnesia as a refractory in furnace building; and the use of magnesia in making pottery.

H. St. C. Deville, H. Schwarz, and F. Knapp noted that magnesium oxide prepared by heating magnesium chloride or nitrate to redness has **hydraulic properties** in that when mixed with a limited quantity of water, it sets rigid like portland cement, and the product is hard enough to scratch marble. On the other hand, magnesia, prepared by calcination for 12 hrs. at a white heat, no longer sets with water, or, if it does, the setting is very slow. A. Ditte also made observations: Magnesia prepared by calcining the nitrate at 350°, when fashioned into rods and spheres with water, remains soft and friable when under water 8 months; that calcined at 440°, hardens under water and in 2 months is like polished marble; that calcined at 560°, also is very hard after standing 2 months under water; while that calcined at 1200° does not harden under water. According to W. C. Anderson, magnesium oxide prepared by gently heating the native carbonate reacts quickly with water, and, when in presence of a limited amount of water, sets to a firm mass. The product obtained by heating similarly the artificial carbonates does not set, although it also appears to slake rapidly with water, but if these carbonates be treated with nitric acid and the resulting nitrate ignited gently, the oxide left will set similarly to that obtained from the native carbonate by heat.

Magnesia gradually absorbs moisture and carbon dioxide from the atm. E. de M. Campbell[13] has measured the **rate of hydration** of magnesium oxide burned at different temp., and selections from his measurements are shown graphically and diagrammatically in Fig. 8. The hydration of magnesium oxide burned between 600° and 800° is practically complete in three days; and a change in the constitution of magnesium oxide sets in between 1000° and 1100°, resulting in a marked decrease in the rate of hydration, and this change becomes more and more marked with rise of burning temp., until, at 1450°, or nearly the temp. employed in burning portland cement, the magnesium oxide combines with

only 61·4 per cent. of the water required for complete hydration. C. Edwards and A. Rigby have measured the rates of hydration of dolomite calcined at different temp., and then exposed to atm. of different degrees of humidity, from which it appears that the lime hydrates faster than the magnesia, and that the higher the temp. of calcination up to about 1150°, the faster the rate of hydration; beyond that temp., the higher the temp. of calcination, the slower the rate of hydration. The subject has also been studied by A. M. Sen, and N. Parravano and C. Mazzetti. The latter found that H. le Chatelier's statement that magnesium oxide undergoes a transformation at about 1600°, and E. de M. Campbell's that it changes at about 1100°, are incorrect. The change occurs at 800°, but very slowly. The presence of impurities in the magnesite modify the transformation—*e.g.* iron oxides accelerate the change. J. W. Mellor showed that there is no definite transformation temp., but that the change proceeds more quickly the higher the temp. of calcination, and each variety of native magnesite has its own specific rate of transformation. The change is possibly a conversion from amorphous to crystalline periclase.

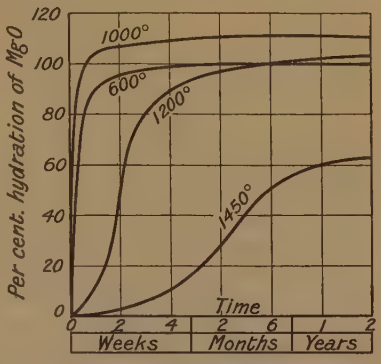

FIG. 8.—Rates of Hydration of Magnesium Oxide Calcined at different Temperatures.

The various determinations of the **solubility** of magnesium oxide or rather hydroxide in *water* are discordant. Reducing the data by the different observers to milligrams of magnesium hydroxide, $Mg(OH)_2$, per litre, J. Dalton [14] gave 62·5 in cold water; R. Kirwan, 126·5 in cold water; O. Henry, 172·4 at 15°; A. Fyfe, 194·5 at ordinary temp., and 27·8 at 100°; R. Fresenius, 27·8 in either cold or boiling water; A. Bineau, 5 to 10 in cold water; F. Kohlrausch and F. Rose, 9 at 18°; A. Dupré and M. Bialas, 8 at 18°; and G. C. Whipple and A. Mayer, 12 at 22°. The wide variations in the results are due to the magnitude of the sources of error in contrast with the magnitude of the constant being measured. These errors are: (i) The solvent action of carbon dioxide dissolved by the water from the air; (ii) the action of water on the glass containing vessels whereby bases are dissolved, and when the solubility is estimated from the alkalinity of the soln., the dissolved alkali introduces a large error; (iii) the presence of such impurities as lime in the magnesia would introduce a large error when lime plus magnesia is regarded as magnesia; and (iv) the uncertainty involved in the assumption that equilibrium is attained since the rates of dissolution of magnesia, prepared in different ways, are very different. The best representative value of the modern determinations of the solubility of magnesia in water is 10 mgrms. of magnesium hydroxide per litre of water at 20°. W. C. Anderson showed that a given oxide, calcined at different temp., dissolves in water at different rates, the rate of soln. being diminished as the temp. of preparation is increased; on the other hand, the extent of this diminution is not the same for oxides obtained from different sources. It is greatest in the case of the oxide obtained from heavy carbonate, less marked in the product from crystal carbonate, and scarcely appreciable in that from light carbonate. The aq. soln. of magnesia is not caustic, but it has an alkaline reaction, changing red litmus blue, etc.

According to H. Precht, a litre of a 2*N*-soln. of *potassium hydroxide* dissolves 16·13 mgrms. of magnesium hydroxide. R. Warington showed that the solubility of magnesium hydroxide is augmented by *ammonium salts*, even in the presence of free ammonia. From experiments on the equilibrium: $Mg(OH)_2+2NH_4Cl \rightleftharpoons MgCl_2+2NH_4OH$, at 10°, J. M. Lovén calculated that the solubility of magnesium hydroxide is $3{\cdot}5\times10^{-4}$ mols per litre; and at 29°, W. Herz and G. Muhs calculated

$2{\cdot}3\times10^{-4}$ mols per litre. Like J. M. Lovén, F. P. Treadwell concludes that the non-precipitation of magnesium hydroxide by ammonia in the presence of ammonium salts is not due to the formation of a complex salt, but solely to the retardation of the dissociation of the ammonium hydroxide by the ammonium chloride according to the law of mass action. W. Herz and G. Muhs give for the solubility of magnesia in ammonium salt soln. at 29°, when the conc. are expressed in grams per litre,

	NH_4Cl					NH_4NO_3	
Ammonium salt . .	4·13	5·67	9·21	13·39	20·86	6·00	14·69
Magnesium hydroxide .	1·43	1·86	2·00	3·15	4·55	1·45	2·43

When warm soln. of ammonium salts are heated with magnesia, ammonia is evolved. R. Warington found *sodium and potassium salts* act similarly in their solvent action on magnesia, but to a less degree. C. J. B. Karsten stated that magnesium hydroxide is insoluble in conc. aq. soln. of many salts—*e.g.* sodium chloride, sulphate or nitrate, barium nitrate and chloride, and potassium nitrate. O. Henry reported that the presence of *calcium hydroxide, calcium sulphate,* or *potassium sulphate* does not interfere with the solvent action of water on magnesia. In general, however, F. K. Cameron and J. M. Bell say that *the solubility of magnesia in water is augmented by various salts, including magnesium salts, but is depressed by the alkali hydroxides.* E. Maigret found the presence of the free base, sodium hydroxide, lowers the solubility of magnesia in a soln. of sodium chloride. Expressing conc. in grams per litre,

	0·8 grm. NaOH			4·0 grms. NaOH			
Sodium chloride . .	125	140	160	125	140	160	grms.
Magnesium hydroxide .	0·07	0·045	nil	0·03	nil	nil	

G. Fleury found the solubility of magnesia in water is increased when *glucose* is present; although C. Bernard and L. Ehrmann ignored this in using sugar soln. to remove lime from magnesia. C. Neuberg and B. Rewald [15] found that magnesia slowly dissolves when shaken for a long time with *methyl alcohol*, forming a typical **magnesia alcosol** which contains in a litre an amount of magnesia corresponding with 4·5 per cent. $Mg_2P_2O_7$, *i.e.* 1·63 per cent. MgO.

Magnesium hydroxide, $Mg(OH)_2$.—The mineral *brucite* was discovered in 1814 by A. Bruce [16] at Hoboken (New Jersey); it was called *talc-hydrate* by C. C. von Leonhard; *magnésie hydratée* by R. J. Haüy, and F. S. Beudant applied the term brucite in 1824. The mineral is found with magnesite and dolomite in serpentine as a result of the decomposition of magnesian silicates. J. Pierce, and T. Nuttall described a fibrous or amianthoidal form of magnesia which was designated *nemalite* or *nematolite*—from *νῆμα*, a fibre. J. D. Whitney, and C. F. Rammelsberg proved its chemical identity with brucite. Magnesium hydroxide is formed during the hydration of magnesium oxide. G. O. Rees [17] stated that magnesia is converted into the hydroxide by moistening it with water, and drying the mass on a water-bath. Colloidal and a readily soluble form of the hydroxide is produced by the action of water or steam at 150° on magnesia. The **colloidal magnesium hydroxide** is readily obtained by adding an excess of potassium or sodium hydroxide to a soln. of a magnesium salt. As remarked by P. Grouvelle,[18] and R. F. Marchand and T. Scheerer, it is difficult to wash the precipitate free from alkalies. H. E. Patten found that magnesium hydroxide does not carry into precipitation with it either chlorine or sulphur trioxide; and at 20°, more than the theoretical amount of potassium hydroxide is required for complete precipitation. The washed and dried hydroxide is a white powder, or, when dried at 100°, is a translucent, coherent, soft brittle mass—presumably in the colloidal state. A. de Schulten prepared crystallized magnesium hydroxide as follows:

12 grms. of magnesium chloride, $MgCl_2$, $6H_2O$, 340 grms. of potassium hydroxide, and 60 c.c. of water, are heated at 212°–220° until the magnesium hydroxide completely dissolves. If the proportion of potash is larger, a lower temp. is sufficient. The liquid is allowed to

cool, and the solid residue treated with water to remove the alkali. The magnesium hydroxide is left undissolved in the form of small, distinct crystals of sp. gr. 2·36 at 15°; these dissolve easily in acids and in warm conc. soln. of ammonium chloride. If soda is used instead of potash, the magnesium hydroxide does not dissolve, but the precipitate rapidly becomes crystalline.

G. Friedel also made crystals of the hydroxide by the action of soda lye on magnesia at 400°, and he considers that this explains the formation of crystals of brucite in boiler deposits, observed by G. A. Kenngott, A. Weisbach, and O. Luedecke.

According to F. Hessenberg,[19] the **crystals** of brucite are trigonal, with $a:c=1:1{\cdot}52078$, and $\alpha=81°\ 12'$. R. Hermann described some crystals of magnesium hydroxide from Texas, Pa., as monoclinic, and called the mineral *texalite*. which would make magnesium hydroxide dimorphous, but this is not yet established because the crystals behave optically like brucite. G. Aminoff calculated from the **X-radiograms** that the elementary parallelopiped has $a=3{\cdot}13$ A., and $c=4{\cdot}75$ A. The **specific gravity** of artificial crystals was found by A. de Schulten to be 2·36 at 15°. For brucite, R. Hermann gave 2·36; W. Beck, 2·376; A. A. Lösch, 2·388; F. R. Mallet, 2·454 at 15°; M. F. Heddle, 2·336–2·37; L. Peruzzi, 2·385 at 17°; and V. von Zepharovich, 2·39. The **hardness** is 2 on Mohs' scale. O. Mügge has studied the **percussion figures** of brucite.

According to J. M. van Bemmelen,[20] the hydroxide passes into the oxide at a temp. below a red heat; it does not lose its combined water in a dry atm. at 350°, but it does so between 350° and dull redness. The hydroxide dried over sulphuric acid without heating, absorbs about 1·6 mols of water when exposed to moist air, but it loses this property if previously heated to 200°, owing to its conversion from the colloidal to the crystalline state. Magnesia obtained at a dull red heat, again takes up $1\frac{1}{2}$ mols of water and one mol of this is retained as water of constitution, $Mg(OH)_2$; if the magnesia has been obtained by ignition at a still higher temp., it is only partially converted into hydroxide in a moist atm., and if calcined 20 hrs. at this temp., it no longer takes up water of constitution. J. Johnston found the **dissociation pressure** of magnesium hydroxide to be:

	35°	53°	74°	100°	147°	c. 160°
Vap. press. . . .	9·2	31·5	92	234	526	760 mm.

At 25°, the press. is $2{\cdot}3\times10^{-3}$ atm., and the dissociation temp. is approximately 160°.

A. des Cloizeaux[21] found brucite had a strong positive **double refraction.** The plate-like crystals of brucite resemble those of gypsum and talc in softness, foliated structure, cleavage and lustre, but gypsum is biaxial, and talc has negative double refraction. M. Bauer gave for the **index of refraction** with red light for the ordinary ray $\omega=1{\cdot}559$, and for the extraordinary ray $\epsilon=1{\cdot}5795$. L. Peruzzi found $\omega=1{\cdot}562$, and $\epsilon=1{\cdot}5827$. M. Bauer, R. Brauns, and H. Rosenbusch have studied the modification in the optical properties of the crystals by strain. U. Panichi found that no change in the optical properties occurred when the crystals were cooled to −190°. W. W. Coblentz,[22] and J. Königsberger studied the **infra-red absorption spectrum** of brucite and noted that gypsum shows an absorption spectrum which is a composite of the bands of water and of anhydrite, while that of brucite is different, thus distinguishing between the water of crystallization of gypsum from the water of constitution of brucite. There is a large band near $2{\cdot}5\mu$ which with higher dispersion is resolved into three bands with maxima at $2{\cdot}5\mu$, $2{\cdot}7\mu$, and 3μ; beyond this region there are no marked bands, while beyond 12μ there is complete opacity. There are depressions in the transmission curve for 5μ, 7μ, $7{\cdot}7\mu$, $8{\cdot}2\mu$, $9{\cdot}7\mu$, and $10{\cdot}8\mu$, but as a whole the curve is conspicuous for the absence of sharp absorption bands.

F. Beijerinck[23] found that the **electrical conductivity** of brucite is nil. W. Hankel found that the crystals exhibit **pyroelectricity,** for, on cooling, the two ends of the principal axis and the adjacent surfaces are electrically negative, while

the corners of the base and the neighbouring surfaces are electrically positive. J. C. Bose studied the absorption of electrical waves by nemalite.

Magnesium peroxide.—C. Weltzien's experiment [24] on the action of hydrogen peroxide on magnesium has already been indicated. R. Haas treated a soln. of a magnesium salt, containing 3 per cent. hydrogen peroxide, with aq. ammonia, and obtained a precipitate which contained some active oxygen, and appeared to have the characteristics of a peroxide. R. Wagnitz patented a preparation made by mixing 50 parts of magnesium hydroxide or hydrocarbonate, moistened with about 5 parts of water, with 10 to 12 parts of sodium peroxide; other modes of mixing were also employed. Undue heating of the mixture should be avoided. F. J. Homeyer also added sodium or barium peroxide to the soln. of a magnesium salt and obtained a product estimated to contain 30 per cent. magnesium dioxide, MgO_2. A. Krause also patented analogous mixtures. O. Ruff and E. Geisel attempted to prepare pure magnesium peroxide by the addition of pure sodium hydroxide to magnesium sulphate soln. in the presence of hydrogen peroxide. Even when a large excess of the latter is used, the precipitate in the moist state has the ratio $MgO : O = 1 : 0{\cdot}67$. Drying the precipitate reduces the proportion of peroxide oxygen, and a product is obtained which has the composition $MgO.MgO_2$, aq. The dried product readily loses oxygen at 25° or 37°, and at atm. press., but even after 22 days the ratio $MgO : O$ was $1 : 0{\cdot}39$, and the ratio appears to remain constant at $1 : 0{\cdot}35$, corresponding roughly with the formula $MgO_2, 3MgO$, aq. The decomposition is more rapid in the presence of water.

E. Merck agitated dried magnesium oxide with anhydrous hydrogen peroxide; the anhydrous solid is easily separated from the water formed in the reaction, and does not require washing. A repetition of the treatment furnishes a peroxide of high degree of purity. F. Hinz used an electrolytic process for preparing magnesium peroxide. The anode compartment of an electrolytic cell is supplied with an aq. (about 20 per cent.) soln. of magnesium or zinc chloride, whilst the cathode compartment contains magnesium or zinc chloride soln. to which hydrogen peroxide has been added; the anode is of platinum or carbon, and the cathode platinum. An e.m.f. of 6 or 7 volts is used in preparing magnesium peroxide, and 2·5 to 3 volts for zinc peroxide. Any free acid formed in the cathode compartment is neutralized by the addition of magnesium or zinc oxide or hydroxide. The reaction presumably progresses $Mg + H_2O_2 + 2H_2O \rightarrow H_2 + Mg(OH)_4$.

The peroxides of the alkaline earths, zinc, and magnesium have attracted some attention on account of their chemical and physiological properties and their use as antiseptics. Magnesium peroxide is a white powder which may be magnesium hydroperoxide, $Mg(OH)_4$; and it usually contains some magnesium hydroxide, and water. R. von Foregger and H. Philipp say "preparations containing certain amounts of available oxygen are more stable than other preparations containing more or less than these." Thus, a product containing 9·2 per cent. of available oxygen seems to be stable, whilst if a product contains less than this it gradually loses its available oxygen, till it reaches 8 per cent. available oxygen, when it again remains stable; and stable products occur containing 6·85 to 6·9 per cent., and also 4·3 per cent. oxygen. The less available oxygen the product contains the more stable it is under atm. conditions. The ordinary product contains about 8 per cent. oxygen and has a sp. gr. of 0·615. Magnesium peroxide has the solubility of 1 part in 14,550 parts of water at 20° C. Suspended in water it loses its available oxygen quicker than zinc peroxide, and slower than calcium or strontium peroxides, but it loses its available oxygen quicker in moist atm. than the other peroxides, as it is apparently more subject to the influence of carbon dioxide. In a dry atm. it is, however, comparatively stable, and can be heated to 160° C. without any loss. It reacts like these other peroxides with acids and certain organic matters.

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§ 7. Magnesium Fluoride

The mineral *sellaïte* is a native magnesium fluoride, MgF_2, which G. Strüver [1] found at Moutiers in France. It forms colourless or white tetragonal crystals of sp. gr. 2·9–3·2; and hardness 5–6. A. and E. Scacchi found some crystals in the lava of the Vesuvian eruption of 1872 which they called *belonesite* or *belonite*, and which were shown by F. Zambonini to be identical with G. Strüver's sellaïte.

J. L. Gay Lussac and L. J. Thénard [2] dissolved magnesium oxide in hydrofluoric acid. J. J. Berzelius prepared magnesium fluoride by treating magnesium carbonate with hydrofluoric acid, or by precipitation from a soln. of magnesium sulphate by potassium fluoride. F. Röder obtained it by melting together 5 parts of magnesium chloride, 4 parts each of sodium fluoride and chloride; on cooling, long needle-like crystals of magnesium fluoride are obtained. H. Moissan made magnesium fluoride by burning the powdered metal in fluorine gas—the combustion proceeds *avec beaucoup d'éclat;* A. Feldmann heated magnesium chloride with calcium fluoride, and digested the product with water acidulated with hydrochloric acid. The product obtained by dissolving the oxide or carbonate in hydrofluoric acid, or by passing gaseous hydrogen fluoride over magnesium oxide, is an amorphous powder which is not converted into crystals either by heating it with dil. hydrochloric acid to 250°, or by the evaporation of its soln. in nitric acid; but, according to A. Cossa, it may be crystallized by cooling the fused fluoride, or by melting it with alkali chlorides—these crystals resemble sellaïte. According to A. Sella, the crystals are tetragonal with the axial ratio $a : c = 1 : 0{\cdot}6596$.

The sp. gr. of artificial crystals of magnesium fluoride, determined by A. Cossa,[3] is 2·857 (12°), and for the natural crystals the sp. gr. vary from G. Strüver's 2·962 to 3·153 (16°); H. G. F. Schröder gives 2·472 as the sp. gr. of the precipitated and calcined powder. The hardness of sellaïte is about the same as apatite, 6. Magnesium fluoride, said E. Beck, has the m.p. 1396°, and it forms a eutectic with 48 per cent. of calcium fluoride, melting at 945°. This eutectic appears to form mixed crystals with up to 17 per cent. of barium fluoride. There is a ternary eutectic with 15 per cent. magnesium fluoride, 15 per cent. calcium fluoride, and 70 per cent. barium fluoride, which melts at 790°; and by adding magnesium oxide, the ternary eutectic is lowered to 764°. According to A. Guntz, the heat of formation $(Mg, F_{2gas}) = 67{\cdot}4$ Cals.; and the thermal values of the reactions $MgSO_4 + 2KF = MgF_{2solid} + K_2SO_{4soln.}$ —0·87 Cal. at 10° when an eq. of the salts are present in two litres of water; $MgO_{ppd.} + 2HF_{soln.} = MgF_{2ppd.} + H_2O + 15{\cdot}2$ Cals. with an eq. of the acid in two litres of water; and $Mg(OH)_{2ppd.} + 2HF_{gas} = MgF_2 + 2H_2O_{solid} + 28{\cdot}4$ Cals.; E. Petersen gives $Mg(OH)_{2aq.} + 2HF_{aq.} = 30{\cdot}12$ Cals. Sellaïte has a feeble refracting power; the double refraction is positive. E. Mallard, A. Sella, and F. Zambonini found for sodium light indices of refraction between $\omega = 1{\cdot}3775$ and 1·379; and $\epsilon = 1{\cdot}3889$ and 1·3897. Warm crystals of sellaïte show a faint violet luminescence with cleavage, a property which is lost by calcination; A. Cossa also found that the natural or artificial crystals give a violet fluorescence when heated after exposure to the arc light. S. Datta studied the three groups of spectral bands of magnesium fluoride.

According to F. Kohlrausch, a litre of water at 18° dissolves 0·076 grm. of MgF_2 by the conductivity method—the specific conductivity of the sat. soln. being 0·000224 at 18°—but the salt is rather more soluble in ammoniacal soln. Magnesium fluoride in many of its properties recalls those of calcium fluoride. J. L. Gay

Lussac and L. J. Thénard found magnesium fluoride is but slightly soluble in acids; and J. J. Berzelius, that it is insoluble in hydrofluoric acid. A. Cossa showed that it is decomposed by conc. sulphuric acid less easily than calcium fluoride; and decomposed by fusion with alkali carbonates more easily than calcium fluoride. L. E. Rivot found it to be insoluble in soln. of ammonium or magnesium salts. The amorphous form, however, is more readily attacked than the crystalline variety. H. Schulze said that magnesium fluoride is not decomposed when calcined in oxygen; A. Tissier, that it is not decomposed by calcium oxide; A. Cossa, that it forms fusible compounds with the sulphates of the alkaline earths, and that when calcined with beryllium or aluminium sulphate it forms the respective fluoride. W. Weldon once recommended the use of magnesium fluoride in the manufacture of soda ash; and it has also been tried as an opacifying agent in the manufacture of glass.

A. Tissier,[4] and M. Netto prepared cubic crystals of **sodium magnesium fluoride,** $NaF.MgF_2$, by boiling magnesium hydroxide with an aq. soln. of sodium fluoride: $3NaF+Mg(OH)_2=2NaOH+NaF.MgF_2$. A. Geuther found crystals of the same product in the slag obtained in the preparation of magnesium silicide by fusing magnesium with sodium fluosilicate and chloride. The compound is decomposed by conc. sulphuric acid, and by milk of lime: $Ca(OH)_2+2NaF.MgF_2=2NaOH+CaF_2+2MgF_2$. M. Netto also made $2NaF.MgF_2$ by fusing hexahydrated magnesium chloride or sulphate with sodium fluoride and chloride.

A. Duboin prepared quadratic prisms of **potassium magnesium fluoride,** $KF.MgF_2$ by extracting with water the slowly cooled cake obtained by fusing a mixture of an excess of potassium fluoride and magnesium oxide at a red heat. The magnesium slowly dissolves in the fused fluoride. The sp. gr. of the insoluble crystals is 2·8 (0°); they are decomposed by sulphuric and hydrochloric acids. If a large proportion of magnesium oxide be used, a hard transparent mass of $2KF.MgF_2$ is formed of sp. gr. 2·7 (0°). It is completely decomposed by hydrochloric and sulphuric acids, and slightly decomposed by the prolonged action of boiling water.

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§ 8. Magnesium Chloride

Magnesium chloride is widely scattered in nature ; it occurs in many mineral waters and in sea-water. The water of the Mediterranean is said to contain a rather larger proportion than the Atlantic Ocean, and *le sel*, which is extracted from the salt gardens of the Mediterranean, has a more bitter taste than *le sel* obtained from those which are concentrated from the waters of the Atlantic. In 1825, T. Monticelli and N. Covelli [1] found *magnesia muriata* in the fumaroles and volcanic vents of Vesuvius ; in 1832, L. Pilla noted its occurrence along with sodium chloride in the crater crusts ; and A. Scacchi found it in the eruptions in 1855 and 1872, and he proposed the name *chloromagnesite*, and assigned to it the formula $MgCl_2.xH_2O$. F. Zambonini considers the magnesium chloride in these deposits is united as a double salt with the alkali chloride. The mineral *bischofite*, hexahydrated magnesium chloride, $MgCl_2.6H_2O$, found in the Stassfurt deposits, was named by C. Ochsenius in honour of G. Bischof. It occurs in the carnallite, kieserite, and salt clay regions, and it is supposed to be a secondary constituent formed by the action of water on carnallite. Magnesium chloride also occurs as *carnallite*, $MgCl_2.KCl.6H_2O$, or $KMgCl_3.6H_2O$; and as *tachyhydrite*, *tachhydrite*, or *tachydrite*, $MgCl_2.CaCl_2.12H_2O$, or $(Ca,Mg)Cl_2.6H_2O$, in the Stassfurt deposits.

J. L. Gay Lussac and L. J. Thénard [2] made anhydrous magnesium chloride by leading chlorine gas over red-hot magnesium oxide. The oxygen simultaneously evolved was attributed to the decomposition of chlorine which they called oxymuriatic acid—according to R. Weber, the reaction proceeds without incandescence, and requires a much higher temp. than is needed for the analogous reaction with lime or baryta. P. S. Curie also made the chloride by passing hydrogen chloride over magnesium sulphide. A. A. B. Bussy and J. J. Berzelius made it by passing chlorine over a red-hot mixture of magnesia and carbon in a porcelain tube—the magnesium chloride collected at the bottom of the tube without sublimation. The De Nordske Saltverker has a modification of this process for working on a large scale. J. von Liebig, R. Bunsen, and J. A. Wanklyn and E. T. Chapman obtained the anhydrous chloride by burning the metal in chlorine gas. According to R. Cowper, if the gas is quite dry magnesium is not attacked by chlorine. J. W. Döbereiner and R. Bunsen obtained the anhydrous chloride by calcining dry ammonium magnesium chloride.

R. Bunsen added sufficient ammonium chloride to a soln. of magnesium carbonate in hydrochloric acid, to prevent the precipitation of magnesium hydroxide when aqua ammonia is added until the soln. is slightly alkaline. Any silica, etc., which separates is filtered off, and the clear liquid is neutralized with hydrochloric acid and evaporated to dryness. The double ammonium and magnesium chloride so obtained is melted at about 460° in a Hessian crucible, in the bottom of which is placed a smaller platinum dish. When the ammonium chloride is all expelled, the magnesium chloride collects in the platinum dish.

According to H. St. C. Deville and H. Caron, and E. Sonstadt, the magnesium chloride so prepared frequently contains nitrogen, and, according to J. B. A. Dumas, magnesium oxide. In a modification of the process, a mixture of magnesium oxide and ammonium chloride is heated, and more ammonium chloride added from time to time. M. M. T. K. Kaisha, and I. Namari and Y. Hiraoka added ammonium chloride and the oxide, hydroxide, carbonate, or oxychloride of magnesium to a fused halide of a more electropositive metal. The product was considered suitable for electrolysis for magnesium.

W. Heap and E. Newbery made anhydrous magnesium chloride by treating the oxide or a salt with a weak acid—carbonate or oxalate—with carbonyl chloride at 500°–600°. A mixture of carbon monoxide and chlorine passed over animal charcoal will serve the same purpose. H. J. Bull used carbon tetrachloride or carbonyl chloride with magnesia, or magnesite ; if dolomite is used, a mixture of calcium and magnesium chlorides is obtained which may be used in electrolysis.

V. M. Goldschmidt chlorinated magnesia in the presence of sulphur or sulphur chlorides free from oxygen, and at 200°–500° found that the reaction went according to the equation: $2MgO+2Cl_2+S=SO_2+2MgCl_2$.

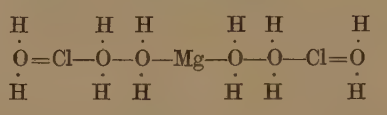
T. W. Richards and H. G. Parker heated the dried ammonium magnesium chloride in a stream of dry hydrogen chloride and obtained magnesium chloride of a high degree of purity. The magnesium chloride soln. used in the preparation of the double salt was purified in the following manner:

> About 500 grms. of magnesium chloride were sat. with hydrogen sulphide, a small amount of ammonia was added, and the whole was allowed to stand in a warm place for several days. To the supernatant liquid after decantation a small quantity of very pure ammonium oxalate was added. The magnesium chloride thus almost wholly freed from calcium was again decanted; and after more ammonium oxalate had been added, the whole was allowed to stand, and the clear liquid was yet once more decanted. The soln. was then evaporated to dryness, and the resulting cake dried in an oven and ignited in a platinum dish. The mixture of magnesium oxide and oxychloride thus formed was washed with the aid of a filter pump for about sixty hours. At the end of this time, although the wash water contained no sodium, the insoluble precipitate was not free from that metal. The precipitate was therefore dissolved in hydrochloric acid, previously distilled in platinum for the purpose, and the soln. was filtered. In order to eliminate the sodium, a portion of the magnesium was precipitated by passing into the soln. a current of ammonia gas. The precipitate formed by this very wasteful process was washed for several days, at the end of which time it was found to be free from any appreciable traces of sodium and potassium, when tested with the spectroscope. The precipitate was then dissolved in hydrochloric acid.

In the laboratory a soln. of magnesium chloride is made by dissolving magnesium oxide or carbonate in hydrochloric acid. It can also be made by a process analogous to that employed by A. J. Balard for separating Glauber's salt from sea-water, namely, by cooling a conc. soln. of magnesium sulphate and sodium chloride whereby sodium sulphate crystallizes out, and magnesium chloride remains in soln. According to L. Michels, the hydrated salt is made from the mother liquor remaining after extracting potassium chloride from the Stassfurt salts; this is evaporated until its sp. gr. is about 1·375, and then allowed to cool and crystallize. The syrupy yellowish-brown mother liquid contains bromides. The crystals, $MgCl_2.6H_2O$, are melted (about 400°), and they are at the same time partially dehydrated and partly oxidized to an oxychloride. The mixture forms some of the magnesium chloride of commerce. Magnesium chloride could be obtained as a by-product in one of W. Weldon's processes for chlorine; and in E. Solvay's ammonio-soda process if magnesium oxide be used to decompose the ammonium chloride. K. S. Boynton and co-workers discuss the recovery of magnesium chloride from sea-water, where it is obtained as a by-product in the extraction of salt. H. H. Dow and E. O. Barstow proposed to remove calcium chloride from magnesium chloride brine by precipitation as calcium sulphate. C. Clerc and A. Nihoul added calcined dolomite in powder to a soln. of magnesium chloride, and found magnesia to be precipitated and calcium chloride to pass into soln.

The hydrated salt cannot be dehydrated without a loss of hydrogen chloride by simple heating. According to R. Brandes, the loss of hydrogen chloride begins at 106°, and, according to H. Grimshaw, at 117° or even lower temp. H. Hof detected the formation of hydrogen chloride at 157° when soln. of magnesium chloride are evaporated under conditions where the superheating of any part of the soln. is prevented. F. P. Dunnington and F. W. Smither say that all but one mol of the water of crystallization can be expelled at 98° without decomposition, and that the principal loss of hydrogen chloride occurs during the expulsion of the residual water. E. Solvay has patented a process in which an approximation is made by heating the hexahydrated salt to 120° until 80 per cent. of the water is expelled; the residue is then much more resistant, and it can be heated to a higher temp. without much loss as hydrogen chloride; or the hexahydrated salt can be heated until about 50 per cent. of the water is expelled, and the molten salt then broken into small fragments and heated between 300° and 400° in a stream of dry air. In the

Salzbergwerk Neu-Stassfurt's process, it is claimed that the hexahydrated salt can be dehydrated without much loss of hydrogen chloride by heating it to about 175° in vacuo. E. Sonstadt and W. Hempel recommended dehydrating the hexahydrated salt in a stream of dry hydrogen chloride. H. J. Bull used a stream of carbon tetrachloride or carbonyl chloride at 500°–600°. H. H. Dow has described a process for dehydrating this salt. If magnesium oxide is once formed, J. B. A. Dumas found it to be difficult to chlorinate subsequently the oxide. F. A. Gooch and F. M. McClenahan say that the passage of hydrogen chloride has no influence on the speed of dehydration of the first third of the water which occurs at 100°, but that it retards the dehydration between 100° and 130°; and accelerates it above 130°. The hydrolytic dissociation of this salt is not very marked below 200° in air or in hydrogen chloride. F. A. Gooch and F. M. McClenahan found that one-third of the combined water can be expelled from the hexahydrated chloride easily without hydrolysis, but the remaining two-thirds can be driven off only when accompanied by hydrogen chloride, and they explain this by assuming that two-thirds of the combined water is more intimately associated in the mol. complex than the remaining third. They illustrate this graphically :



Compare this with the behaviour of hydrated barium and aluminium chlorides.

J. L. Gay Lussac and L. J. Thénard [3] described anhydrous magnesium chloride as forming a white transparent mass of large lustrous **crystals** with a sharp bitter taste. L. Playfair and J. P. Joule found the sp. gr. to be 2·177. H. St. C. Deville and H. Caron say that the salt may be distilled in a current of hydrogen, forming a distillate resembling butter, which forms a mass of crystalline plates on cooling. E. E. Somermeier found the heat of dissolution of a gram-atom of magnesium in $HCl+19{\cdot}15H_2O$ to be 111·40 Cals. The **melting point** is 708°, according to T. Carnelley, and the f.p. 711°, according to O. Menge. J. Thomsen gives the **heat of formation,** (Mg, Cl_2), 151·01 Cals.; (Mg, Cl_2, aq.), 186·93 Cals.; ($MgCl_2$, aq.), 35·92 Cals.; (Mg, Cl_2, 6aq.), 133·98 Cals.; ($MgCl_2$, 6aq.), 32·97 Cals.; $Mg(OH)_{2aq.}+2HCl_{aq.}=27{\cdot}69$ Cals. G. F. Hüttig gave 2·325 at 25°/4°, for the **specific gravity** of anhydrous magnesium chloride, 2·316 for that of the unmelted and porous salt; and, assuming the sp. gr. is 2·320, W. Biltz gives the mol. vol. 41·05. The **heat of solution** of $MgCl_2.6H_2O$ in 400 mols. of water is 2·95 Cals., and P. Sabatier gives the ht. of soln. of $MgCl_2.6H_2O$ at 19·6° as 6·4 Cals. M. Berthelot and L. Ilosvay de N. Ilosva give for the heat of soln. of magnesium chloride, $MgCl_2$ at $\theta°$, $35480+0{\cdot}0000796(\theta-15°)$; and for $MgCl_2.6H_2O$, $2800+0{\cdot}000025(\theta-15°)$. R. Görgey found for sodium light the **indices of refraction** $\alpha=1{\cdot}495$; $\beta=1{\cdot}507$; and $\gamma=1{\cdot}58$. W. Hampe says that the molten salt is a good conductor of electricity.

According to H. Schulze,[4] magnesium chloride forms magnesium oxide when calcined in oxygen. The reaction has been discussed in connection with the preparation of chlorine, or of hydrogen chloride. F. Haber and F. Fleischmann represent the equilibrium constant K_p of the reaction : $2MgCl_2+O_2 \rightleftharpoons 2MgO+2Cl_2$, by the expression $\log_{10} K_p=-1950T^{-1}-1{\cdot}87 \log_{10} T+7{\cdot}01$, where K_p is equal to $p/p_0^{\frac{1}{2}}$, where p denotes the partial press. of the chlorine, and p_0 that of the oxygen. According to W. Moldenhauer, the following are the values of K_p and the corresponding percentage amounts of oxygen and chlorine by volume calculated from the conc. of oxygen $C_0=100-C$, where C is the conc. of the chlorine; hence $K_p=C/(100-C)^{\frac{1}{2}}$:

	50°	150°	250°	350°	450°	550°	650°	750°
K_p . . .	0·03	0·4	1·9	5·3	10·6	17·4	25·3	35·9
Chlorine . .	0·3	4·0	17·6	40·8	63·5	79·3	88·0	93·3
Oxygen . .	99·7	96·0	82·4	59·2	36·5	20·7	12·0	6·7

The equilibrium at the lower temp. is attained very slowly; the values below 350° are computed by extrapolation in the formula; the equilibrium curve is shown in Fig. 9, the dotted curve shows the results obtained after 10 hrs. heating and illustrates the tardiness with which equilibrium is attained at the lower temp. The heats of formation of magnesium chloride is 151 Cals., and of magnesium oxide, 143·3; consequently the thermal value of the reaction: $MgCl_2+O=MgO+Cl_2$

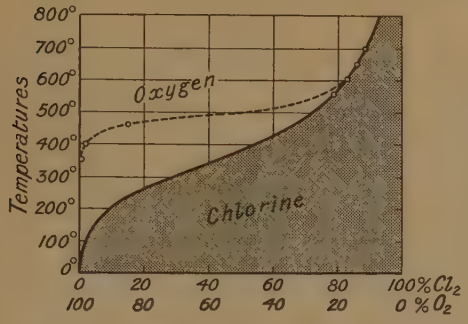


FIG. 9.—Equilibrium Conditions in $2MgCl_2+O_2=2MgO+2Cl_2$.

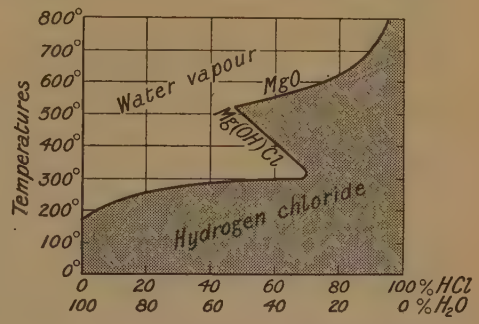


FIG. 10.—Equilibrium Conditions in the Reaction: $MgCl_2+H_2O$.

—7·7 Cals. at constant press. The value computed from J. H. van't Hoff's equation between 550° and 650° is:

$$\log\frac{K_1}{K_2}=\frac{Q}{2}\left(\frac{1}{T_1}-\frac{1}{T_2}\right);\text{ or }\log\frac{25{\cdot}3}{17{\cdot}4}=\frac{Q}{2}\left(\frac{1}{923}-\frac{1}{823}\right)$$

or Q=—5600 cals. at about 600°, and at room temp., about —7400 cals. J. W. Döbereiner also showed that magnesium chloride is decomposed when heated with potassium chlorate; and by water vapour.

The action of steam on magnesium chloride has been studied by W. Moldenhauer. The composition of the solid residue at different temp. when magnesium chloride is heated with steam is:

	250°	300°	350°	400°	600°
$MgCl_2$	78·2	72·9	77·7	64·3	44·8
MgO	5·1	17·6	15·0	24·3	54·4
H_2O	16·7	9·5	7·3	11·6	0·8

The composition of the gases in percentages of volume:

	183°	213°	250°	300°	350°	400°	500°	600°	700°
HCl	0·8	7·9	21·0	66·5	69·4	62·15	50·2	75·1	90·2
H_2O	99·2	92·1	79·0	33·5	30·3	37·85	49·8	24·9	9·8

The results are plotted in Fig. 10. W. Moldenhauer attributes the phenomena to changes in the composition, the solid phase being such that the amount of hydrogen chloride in the reaction between steam and magnesium chloride steadily increases up to a maximum between 300° and 350°; between 350° and 505°, magnesium hydroxychloride, Mg(OH)Cl, is formed by a reaction which decreases the proportion of hydrogen chloride in the system; the equilibrium reaction is then represented, $MgCl_2+H_2O\rightleftharpoons Mg(OH)Cl+HCl$; between 500° and 510°, the hydroxychloride, Mg(OH)Cl, decomposes; and above this temp., the equilibrium reaction is: $MgCl_2+H_2O\rightleftharpoons 2HCl+MgO$. The curve between 200° and 350° is uncertain because of the long time required to attain equilibrium. The equilibrium constant K in the reaction: $MgCl_2+H_2O\rightleftharpoons Mg(OH)Cl+HCl$, when $K=[HCl]/[H_2O]$, where the bracketed terms represent concentrations, is K=1·64 at 400°, and K=1·01 at 500°, so that from J. H. van't Hoff's equation, the heat of the reaction between these temp. is 5100 cals. Similarly, the equilibrium constant K' in the reaction $MgCl_2+H_2O$

$=MgO+2HCl$, when $K=[HCl]^2/[H_2O]$ is $K=226{\cdot}5$ at 600°, and $K=830{\cdot}2$ at 700°; and the computed heat of the reaction is —22000 cals. on the imperfect assumption that the sp. ht. of the reacting substances are independent of temp. From the thermochemical data, $MgCl_2+H_2O=MgO+2HCl$, $-151000-57000+143300+44000=-20700$ cals. The reaction involving the formation of the intermediate Mg(OH)Cl is exothermal, the other reaction at the higher temp. being endothermal.

The **solubility** of magnesium chloride expressed in grams of $MgCl_2$ per 100 grms. of soln. between 0° and 100°, where the solid phase is $MgCl_2.6H_2O$, is

	0°	10°	20°	40°	60°	80°	100°
$MgCl_2$ . .	34·5	34·9	35·3	36·5	37·9	39·8	42·2

The solubility curve covering the range between 50° and 200° is illustrated in Fig. 11. The solubility with ice as the solid phase falls from 11·1 per cent. at —10° to the eutectic *B* with the solubility 20·6 per cent. at —33·6°; when the solid phase is a mixture of ice and $MgCl_2.12H_2O$; the solubility with $MgCl_2.12H_2O$ as the solid phase then rises to 31·6 per cent. at —16·8°, *C*, where the solid phase is a mixture of $MgCl_2.12H_2O$ and α-$MgCl_2.8H_2O$; at —17·4°, *H*, solubility 32·3 per cent. the solid phases are $MgCl_2.12H_2O$ and β-$MgCl_2.8H_2O$; at —19·4°, *K*, solubility 33·3 per cent., the solid phases are $MgCl_2.12H_2O$ and $MgCl_2.6H_2O$; at —9·6°, *J*, solubility 34·9 per cent., the solid phases are β-$MgCl_2.8H_2O$ and $MgCl_2.6H_2O$; at —3·4°, *E*, solubility 34·4 per cent., the solid phases are α-$MgCl_2.8H_2O$ and $MgCl_2.6H_2O$, and the last-named salt is the solid phase from —3·4° to 116·7°, *F*, when the solubility is 46·2 per cent., and the solid phases are $MgCl_2.6H_2O$ and $MgCl_2.4H_2O$. At 152·6°, the solubility is 49·1 per cent., at 181·5°, *G*, solubility 55·8 per cent., the solid phases are $MgCl_2.4H_2O$ and $MgCl_2.2H_2O$. At 186° the solubility is 56·1 per cent., and the solid phase is $MgCl_2.2H_2O$. The maximum in the curve at —16·4°, *D*, represents the m.p. of $MgCl_2.12H_2O$. The system at *H*, *J*, *K*, is not stable and represent undercooled soln.

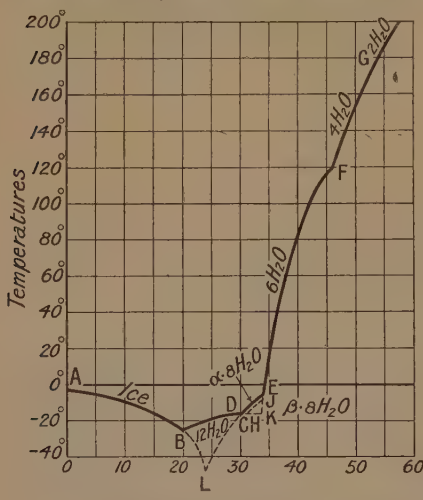


Fig. 11.—Solubility Curves of Magnesium Chloride.

There are at least six different hydrates of magnesium chloride, indicated in Fig. 11. J. H. van't Hoff and W. Meyerhoffer [5] found that **dodecahydrated magnesium chloride,** $MgCl_2.12H_2O$, is formed when a soln. with more than 12 and less than 20 mols of water *per* mol of $MgCl_2$, is cooled to —30° or —35°; or by adding a piece of solid carbon dioxide to an under-cooled soln. $MgCl_2+12H_2O$ at —20°. A. Bogorodsky cooled a soln. of $MgCl_2+10H_2O$ at —20°, and added a little of a soln. $MgCl_2+12H_2O$ cooled below —20°. This salt melts at —16·7° to a clear liquid. The crystals are lighter than the mother liquid, says A. Bogorodsky, and it is not usual for an increase in volume to be observed in the formation of a hydrate. J. H. van't Hoff and W. Meyerhoffer prepared **octohydrated magnesium chloride,** $MgCl_2.8H_2O$, by allowing a sat. soln. of $MgCl_2.6H_2O$ to stand in contact with the solid phase between —15° and —20°; or by cooling a soln. of $MgCl_2+10H_2O$ to —20°, and removing the mass from the freezing mixture, the dodecahydrated salt disappears and the octahydrated salt remains as a coarse crystalline powder which when mixed with the original soln., and cooled to —10° or —12°, forms thick crystalline plates, which decompose at —3·4°; A. Bogorodsky says —9·8°. The

range of its existence extends from −16·7° to −3·4°. **Hexahydrated magnesium chloride,** $MgCl_2.6H_2O$, crystallizes from aq. soln. between −3·4° and 116·67°. According to J. C. G. de Marignac, it forms prismatic monoclinic crystals with axial ratios $a:b:c=1·348:1:0·818$, and $\beta=96°\ 39'$. E. Filhol gives the sp. gr. 1·558 at ordinary temp., and for bischofite, C. Ochsenius gives 1·65; at −188°, J. Dewar found a sp. gr. 1·6039, and he computes the mean coeff. of thermal expansion between 17° and −188° to be 0·0001072. J. H. van't Hoff and H. M. Dawson have examined the lowering of the f.p. of this salt in the presence of ammonium and alkali chlorides; with potassium sulphate there is a raising of the f.p. owing to the formation of kieserite; hexahydrated magnesium bromide forms mixed crystals with hexahydrated magnesium chloride. The crystals deliquesce in air, and W. Müller-Erzbach found the vap. press. to be from 0·012 to 0·016 of that of pure water. P. Bary states that the crystals are phosphorescent when exposed to Röntgen's or Becquerel's rays. H. Davy noted that when this salt is dehydrated, it loses hydrogen chloride, forming magnesium oxide along with the chloride. According to R. Brandes, the crystals begin to lose hydrogen chloride at 106°, they partially melt at 112°, and completely melt at 119°. C. Przibylla gives 116°—118° for the m.p. of bischofite. The phenomena attending the dehydration of this salt have been previously discussed. H. Lescœur prepared **tetrahydrated magnesium chloride,** $MgCl_2.4H_2O$, by passing hydrogen chloride into a soln. of magnesium chloride; P. Sabatier, and W. Müller-Erzbach, by exposing the hexahydrated salt to a dry atm.; J. H. van't Hoff and W. Meyerhoffer, by drying the hexahydrated salt at 100° to a constant weight; or by melting the hexahydrated salt at 130° in a current of air; when the composition approximates to $MgCl_2+5H_2O$, cooling slowly to 117°; warming to 150° and pouring off the mother liquid. A. Ditte made **dihydrated magnesium chloride,** $MgCl_2.2H_2O$, by saturating with hydrogen chloride a water-cooled soln. of magnesium chloride; and by adding anhydrous magnesium chloride to conc. hydrochloric acid without allowing the temp. to rise. J. H. van't Hoff and W. Meyerhoffer made the dihydrated salt by passing dry hydrogen chloride over the tetrahydrated salt at 140°. The crystalline plates are very deliquescent, and, according to W. Müller-Erzbach, have 0·0013th of the vap. press. of water. W. Moldenhauer made **monohydrated magnesium chloride,** $MgCl_2.H_2O$, by passing hydrogen chloride over the hexahydrated-salt for 4–6 hrs. at 135° until there is no further loss in weight; the same result was obtained by 12–14 hrs. heating at 110°.

The **specific gravity** of aq. soln. of magnesium chloride has been determined by D. I. Mendeléeff,[6] R. Engel, P. Kremers, H. Schiff, A. C. Oudemans, and G. T. Gerlach at 15°, and by O. Pulvermacher, H. T. Barnes and A. P. Scott, at 0° and 20°. According to G. T. Gerlach, at 15°,

Per cent. $MgCl_2$.	1	5	10	15	20	25	30	35
Sp. gr. . .	1·0084	1·0412	1·0859	1·1311	1·1780	1·2273	1·2794	1·3340

W. Biltz gave 2·325 at 25°/4° for the sp. gr. of fused magnesium chloride, and 2·316 for the unfused porous salt. According to G. J. W. Bremer, an empirical relation between the sp. gr. D and the percentage composition p is $D=1+0·0091729p+0·00005507p^2$; and the sp. gr. D at the temp. $\theta°$, is $D=D_0(1-a\theta-b\theta^2)$, where D_0 represents the sp. gr. at 0°, and a and b constants, the former of which is greater in value and the latter smaller in value the more conc. the soln. The expansion curves of the different soln. intersect at approximately 60°. According to N. A. Tschernay, unit volume of a soln. $MgCl_2+50H_2O$ at $\theta°$ becomes $v=1+0·0001394\theta+0·0000028892\theta^2$, and for $MgCl_2+100H_2O$, $v=1+0·0000688\theta+0·0_53922\theta^2$. J. Wagner's values for the **viscosities** of $\frac{1}{8}N$-, $\frac{1}{4}N$-, $\frac{1}{2}N$-, and N-soln. of magnesium chloride are respectively 1·026, 1·0445, 1·0940, and 1·2015—water unity. O. Pulvermacher also made some measurements. F. E. Bartell and O. E. Madison studied the **osmosis** of soln. of magnesium chloride through animal membranes; and F. E. Bartell and L. B. Sims, through collodion. F. E. Bartell and D. C. Carpenter also measured the rate of osmosis.

According to J. C. G. de Marignac,[7] the **specific heat** at 22·52° of a soln. of one mol of magnesium chloride in n mols of water is:

n	15	25	50	100	$200H_2O$
Sp. ht.	0·6824	0·7716	0·8665	0·9235	0·9594
Mol. ht.	249·4	421·0	862	1750	3545

G. Jäger found the **heat conductivities** of 11, 14·5, 22, and 29 per cent. soln. of magnesium chloride are respectively 94·9, 91·7, 89·0, and 85·4 (water=100). According to W. Müller-Erzbach, the **vapour pressure** of a sat. soln. of magnesium chloride is about 0·27th that of water. S. Skinner has measured the **boiling points** of aq. and alcoholic soln. of magnesium chloride; and E. M. Baker and V. H. Waite found that U. Dührung's rule applies to the boiling of aq. soln. of magnesium chloride. H. C. Jones and F. H. Getman, and J. H. van't Hoff measured the **freezing points** of the soln.

The refraction and dispersion of soln. of magnesium chloride have been investigated by P. Barbier and L. Roux.[8] For the difference between the **refractive index** of the soln., μ, and that of water, μ_0, for soln. with $\frac{1}{2}MgCl_2$ per v litres, D. Dijken found when $v=1$, $\mu-\mu_0=0{\cdot}011957$; and when $v=128$, $\mu-\mu_0=0{\cdot}0001013$. O. Pulvermacher measured the refractive index of soln. of magnesium chloride. The **electrical conductivity** has been measured by S. Arrhenius,[9] P. Walden, and others. H. C. Jones and co-workers found for the mol. conductivity, μ, and the percentage **degree of ionization,** α, of soln. of magnesium chloride with a mol of the salt in v litres of water:

v	4	8	32	128	512	2048	4096
$\mu_{0°}$	80·2	87·6	99·9	110·3	115·7	120·3	123·5
$\mu_{65°}$	280·6	303·8	364·8	401·6	433·1	465·6	—
$\alpha_{0°}$	64·9	70·9	80·9	89·2	93·7	97·3	100·0
$\alpha_{65°}$	60·3	65·3	78·4	86·3	93·0	100·0	—

The temp. coeff. of the conductivity were also computed by H. C. Jones and A. P. West; and the degree of ionization, by G. Kümmell, and K. Drücker. S. Arrhenius computed the **heat of ionization** in a 0·1 eq. soln. at 35° to be —651 cals. Data for the **transport numbers** of the ions have been measured by W. Hittorf, W. Bein, A. Chassy, and B. D. Steele; and S. von Lasczynsky and S. von Gorsky worked with soln. of magnesium chloride in pyridine. F. E. Bartell and D. C. Carpenter measured the **difference of potential** of water and soln. of magnesium chloride separated by a permeable membrane. S. Meyer gave $-0{\cdot}420\times10^{-6}$ units per grm. or $-0{\cdot}044\times10^{-6}$ units per mol for the **magnetic susceptibility** of anhydrous magnesium chloride, and for the hexahydrated salt, $-0{\cdot}347\times10^{-6}$ units per grm. or $-0{\cdot}092\times10^{-6}$ units per mol.

According to F. Margueritte,[10] gaseous *hydrogen chloride* does not precipitate magnesium chloride from its aq. soln., but R. Engel, and A. Ditte showed that this statement is erroneous; the solubility of magnesium chloride is considerably diminished by hydrogen chloride. Expressing the concentrations in grams per 100 c.c. of soln., R. Engel found at 0°,

Per cent. HCl	0	1·49	3·46	6·20	10·39	5·31	21·42	27·71
Per cent. $MgCl_2$	47·42	45·48	42·86	39·30	33·83	28·64	22·03	15·20

and a soln. sat. with hydrogen chloride dissolves 6·5 per cent. of magnesium chloride. The solubility of magnesium chloride in the presence of other salts has been investigated by R. Löwenherz[11] and by J. H. van't Hoff and co-workers in connection with their studies on the Stassfurt deposits.

Alcohol of sp. gr. 0·90 and 0·871 dissolves respectively 20 and 50 parts of magnesium chloride per 100 c.c. of solvent. S. E. Simon[12] found that heat is evolved when anhydrous magnesium chloride is allowed to act on dry methyl or ethyl alcohol, and on cooling the soln. with a freezing mixture compounds with alcohol

of crystallization separate in deliquescent crystals—*e.g.* **magnesium chloride hexa-methyl-alcoholate,** $MgCl_2.6CH_3OH$; and **magnesium chloride hexa-ethyl-alcoholate,** $MgCl_2.6C_2H_5OH$. L. Kahlenberg and F. C. Kraushoff find the very low solubility of magnesium chloride in anhydrous *pyridine* and its greater solubility in pyridine with 3 or 4 per cent. of water resembles that of calcium and strontium chlorides in the same menstruum.

According to W. S. Clark,[13] magnesium chloride volatilizes when heated in a stream of *ammonia*, leaving a residue of magnesium oxide; the sublimate is **magnesium tetrammino-chloride,** $MgCl_2.4NH_3$, which on exposure decomposes rapidly with the loss of ammonia, but which can be sublimed in an atm. of ammonia. **Magnesium hexammino-chloride,** $MgCl_2.6NH_3$, analogous with calcium hexammino-chloride, was made by F. Ephraim; according to C. Matignon, the heat of dissociation into **magnesium diammino-chloride,** $MgCl_2.2NH_3$, and ammonia at 142° is 13·07 Cals. According to W. Biltz and G. F. Hüttig, the dissociation press. of the hexammines could not be determined because of the formation of mixed crystals or solid soln. of two ammines. G. Spacu and R. Ripan obtained a colourless crystalline powder of **magnesium pentammino-aquachloride,** $[Mg(NH_3)_5H_2O]Cl_2$, by passing ammonia into an alcoholic soln. of magnesium chloride at ordinary temp. W. Biltz and G. F. Hüttig found that the heat of formation and absolute temp. at which the dissociation press. of magnesium diammino-chloride is 100 mm. are respectively 17·9 Cals. and 495°; similarly for **magnesium ammino-chloride,** $Mg(NH_3)Cl_2$, 20·8 Cals. and 573°; G. N. Antonoff made the double compound of magnesium chloride with hydroxylamine, **magnesium hydroxylamine chloride,** $MgCl_2.2NH_2OH.2H_2O$. H. Niggemann found that when a mixture of air and ammonia was passed into a soln. of 50 grms. of hexahydrated magnesium chloride in 50 c.c. of water at 90°, a precipitate of magnesium hydroxide appeared in about 15 mins. The soln. still contained 40·5 grms. of $MgCl_2.6H_2O$ when sat. with ammonia. A mixture of ammonia and carbon dioxide gave an immediate precipitation of magnesium carbonate. G. Spacu made complex salts of magnesium chloride with pyridine and triethylene diammine.

The ready hydrolysis of magnesium chloride soln., as in the case of soln. of beryllium chloride, has led to the production of a number of basic chlorides or **magnesium oxychlorides.** The arguments for the individuality of these products have been based on chemical analyses and are not therefore satisfactory in the light of our present knowledge.[14] The crystalline precipitate, deposited by ammoniacal soln. of magnesium chloride, after washing with water gave G. E. Davis numbers in agreement with $5MgO.MgCl_2.13H_2O$; G. Krause obtained a product $10MgO.MgCl_2.18H_2O$; and C. Bender, $5MgO.MgCl_2.xH_2O$, and $9MgCl_2.xH_2O$. G. André found that needle-like crystals of a product $MgO.MgCl_2.16H_2O$ separate when a boiling soln. of 400 grms. of hexahydrated magnesium chloride and 20 grms. of magnesium oxide in 500 grms. of water is filtered, and allowed to stand 24 hrs. When the crystals are dried in vacuo, they have the composition $MgO.MgCl_2.H_2O$. The crystals are decomposed by water and alcohol. The product $MgO.MgCl_2.H_2O$ can be resymbolized $Mg(OH)_2.MgCl_2$, or Mg(OH)Cl, thus recalling W. Moldenhauer's intermediate product in the action of steam on magnesium chloride between 350° and 500°. The product $MgO.MgCl_2$ prepared by calcining to 300° an intimate mixture of eq. proportions of magnesium oxide and ammonium magnesium chloride, can also be symbolized Cl—Mg—O—Mg—Cl. G. André calculates the heats of formation ($MgO.MgCl_2$) to be 7·72 Cals.; ($MgO.MgCl_2+6H_2O_{solid}$), 1·68 Cals.; ($MgO.MgCl_2+16H_2O$), 1·58 Cals.; and ($MgCl_2+Mg(OH)_2+6H_2O_{liquid}$), 13·7 Cals. A mol of the product $MgO.MgCl_2.6H_2O$ dissolves at 9° in dil. hydrochloric acid containing two mols of HCl, with the evolution of 18 Cals.; and under the same conditions, $MgO.MgCl_2.16H_2O$ develops 11 Cals. Since the magnesium oxychlorides are decomposed by washing preparatory to the analysis, and if not washed, they will be contaminated with mother liquid, W. O. Robinson and W. H. Waggaman attempted to determine the composition of the basic chlorides, and the ranges of

conc. of the soln. over which they can exist, by studying *the solubility of magnesium hydroxide in solutions of magnesium chloride* of different conc. The percentage amounts of magnesium oxide present in soln. of magnesium chloride at 25°, are as follows :

Per cent. MgCl .	2·36	6·79	13·14	22·04	28·34	30·04	34·22
MgO .	0·00008	0·00048	0·00115	0·00245	0·00230	0·00250	0·0030

The detailed results show that at 25°, up to a conc. of about 10 grms. $MgCl_2$ per 100 c.c. of soln., the solid is an indefinite solid soln. of magnesium oxide and chloride, and water, and from that conc. up to a sat. soln. of magnesium chloride, the solid phase is a basic magnesium chloride $2MgO.HCl.5H_2O$, that is, $3MgO.MgCl_2.11H_2O$, or still differently expressed :

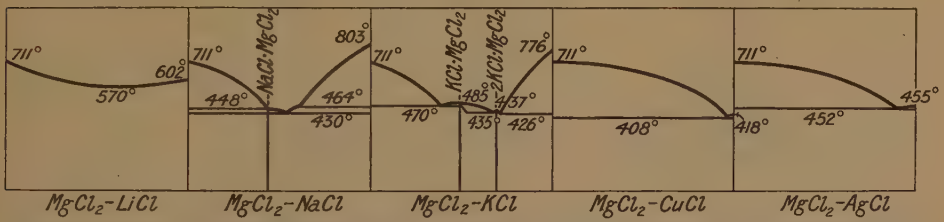
$$O<\begin{matrix}Mg—OH\\Mg—Cl\end{matrix}5H_2O \quad .$$

The so-called *Sorel's magnesia cement* was described by E. Sorel [15] in 1867, and it is made by mixing calcined magnesia with an aq. soln. of magnesium chloride of sp. gr. 1·16 to 1·26. A mixture of finely powdered, dry, calcined magnesite and dry magnesium chloride—which can be preserved in sealed tin vessels—furnishes the same result when mixed with water. The two substances apparently unite with the development of heat, forming what is presumably a magnesium oxychloride, and A. Krieger, E. Luhmann, and L. Preussner have shown that the resulting cement is a mass of minute interlacing crystals. It is supposed that the magnesium chloride and oxide react in soln., forming a supersat. soln. of oxychloride from which crystals are deposited as in the setting of plaster of Paris. Various formulæ have been assigned to the oxychloride. Taking the mol. ratio $MgCl_2$: MgO : H_2O, C. Bender gave 1 : 5 : 17 ; G. E. Davis, 1 : 5 : 13 ; and G. Krause 1 : 10 : 14 when dried at 110° and 1 : 10 : 18 when air-dried. The cement is used for cementing glass and metal, and for making artificial stones, etc.—*e.g.* the so-called *xylolith* is a mixture of sawdust, cement, and water. Several methods of preparing the mixture have been patented—*e.g.* by O. Kraner, F. M. Lyte and J. G. Tatters, etc. F. M. Lyte and J. G. Tatters heated to 300° an intimate mixture of ammonium magnesium chloride, $NH_4Cl.MgCl_2$, with one-fifth of its weight of magnesium oxide ; the residue contained a little less magnesium oxide than corresponded with the formula $MgO.MgCl_2$. A great many modifications have been patented with calcium or barium compounds as accessory constituents, and with starch, gelatinous silica, etc., admixed with the soln. of magnesium chloride. Prolonged treatment of the cement with boiling water dissolves magnesium chloride leaving behind hard magnesium oxide. M. Y. Seaton and co-workers have discussed the action of free lime on the cement.

In 1789, A. F. de Fourcroy [16] showed that ammonium magnesium chloride could be crystallized from a mixed soln. of the component salts ; and K. von Hauer purified the salt by crystallization. The analyses corresponded with the formula for **hexahydrated ammonium magnesium chloride,** $NH_4Cl.MgCl_2.6H_2O$, or *hexahydrated ammonium trichloro-magnesiate,* $NH_4MgCl_3.6H_2O$; also called *ammonium carnallite.* C. H. Pfaff obtained crystals of the same salt by evaporating the filtrate from the precipitate obtained by treating a soln. of magnesium chloride with an excess of ammonia ; and O. Hautz, by similarly treating the liquid remaining after shaking magnesium oxide with a cold aq. soln. of ammonium chloride. J. C. G. de Marignac found that the double pyramidal rhombic crystals have the axial ratios $a : b : c = 1·0295 : 1 : 0·7220$. Potassium and ammonium carnallites form solid soln. with one another. C. H. D. Bödeker's value for the sp. gr. is 1·456. O. Hautz found the salt loses 10·9 per cent. of water at 100°, and 31·15 per cent. ($4H_2O$) at 135°. The crystals are deliquescent and melt when heated, losing first water, and then ammonium chloride ; finally, magnesium chloride alone remains. The salt is sparingly soluble in water ; and the electrical conductivity of aq. soln. has been investigated by H. C. Jones and N. Knight. M. Berthelot and G. André reported a crystalline salt, $2NH_4Cl.5MgCl_2.33H_2O$; and G. Linck, $2NH_4Cl.3MgCl_2.20H_2O$.

C. Sandonnini [17] found that lithium and magnesium chlorides form solid soln. in all proportions, and that these are stable at low temp. The f.p. curve, Fig. 12, shows a minimum with about 40 molar per cent. $MgCl_2$, at 570°. O. Menge obtained the results shown in Fig. 13, for the f.p. curve of the binary mixtures indicated. A

mixture of sodium and magnesium chlorides has a eutectic at 430° and 55 per cent. of NaCl, and two breaks, one corresponding with sodium magnesium trichloride, $NaCl.MgCl_2$, and the other with a compound of uncertain composition. K. Scholich also obtained the two compounds $NaCl.MgCl_2$ and $2NaCl.MgCl_2$. There is some doubt about the existence of the hydrated sodium magnesium trichloride, $NaCl.MgCl_2.xH_2O$. A. B. Poggiale, and A. de Schulten mention this salt, but C. J. B. Karsten, A. J. Balard, and J. N. von Fuchs were unable to dissolve sodium chloride in a soln. of magnesium chloride ; and they found that on cooling a boiling sat. soln. of the two salts, crystals of sodium chloride alone separated out. C. Schräder obtained only mixtures of the component salts by passing hydrogen chloride into soln. of magnesium chloride with sodium or potassium chloride.



FIGS. 12 to 16.—Freezing-point Curves of Binary Systems of Magnesium Chloride with Lithium, Sodium, Potassium, Cuprous, and Silver Chlorides.

O. Menge found the f.p. curve of mixtures of magnesium and potassium chlorides has two maxima, Fig. 14, at 485° and 437° corresponding respectively with the m.p. of potassium magnesium trichloride, $KCl.MgCl_2$, and potassium magnesium tetrachloride, $2KCl.MgCl_2$. The existence of these compounds was confirmed by a microscopic examination of the products. J. Valentin obtained only $MgCl_2.KCl$ on the f.p. curve, and K. Scholich could confirm only the same compound ; he studied the ternary system $MgCl_2$-KCl-NaCl. The solubility of magnesium chloride in soln. of potassium chloride was measured by H. Precht and B. Wittjen, J. H. van't Hoff and W. Meyerhoffer, W. Feit and C. Przibylla, and W. B. Lee and A. C. Egerton. W. B. Lee and A. C. Egerton studied the ternary system KCl-$MgCl_2$-H_2O at 25°. Hexahydrated **potassium magnesium trichloride,** $KCl.MgCl_2.6H_2O$, or hexahydrated *potassium trichloro-magnesiate*, $KMgCl_3.6H_2O$, occurs in the Stassfurt and other salt deposits. H. Rose [18] identified the mineral in the Stassfurt deposits with the double salt which J. von Liebig had found to be deposited from the mother liquors of the brines from the Salzhausen during a winter's cold, and which A. Marcet had previously obtained from the mother liquors in the evaporation of sea-water. In order to indicate that the double salt occurs as a mineral species, H. Rose named it **carnallite,** in honour of R. von Carnall. C. F. Rammelsberg thought that the double salt deposited from mixed soln. of the component salts belonged to the hexagonal system, but J. C. G. de Marignac, and A. des Cloizeaux showed that the artificial, and A. des Cloizeaux, F. Hessenberg, and C. Busz that the natural, crystals belong to the rhombic system, and have axial ratios $a : b : c = 0{\cdot}59304 : 1 : 0{\cdot}69758$. F. Bischof's value for the sp. gr. of natural carnallite is 1·615 ; E. Reichardt's, 1·60 ; and C. Przibylla's, as a mean of eleven determinations at 19·4° (water at 4° unity), with the weighings reduced to those in vacuo, 1·6018. H. H. Kunze studied the sp. gr. and the m.p. of mixtures of carnallite and potassium chloride. J. H. van't Hoff and W. Meyerhoffer found the m.p. in a sealed tube to be 265°. The double refraction is strong and positive ; and C. Busz found the indices of refraction in sodium light to be $\alpha = 1{\cdot}46658$; $\beta = 1{\cdot}47529$; $\gamma = 1{\cdot}49371$. According to F. Beijerinck, carnallite is a non-conductor of electricity. F. Rüdorff examined the diffusion of soln. of carnallite ; and H. H. Kunze, H. C. Jones and N. Knight their electrical conductivity.

J. von Liebig [19] noticed that the crystals of carnallite deliquesce and then

decompose on exposure to air leaving a residue of potassium chloride, and magnesium chloride in soln. ; and A. Marcet, that alcohol extracts magnesium chloride leaving behind potassium chloride. Carnallite is thus partly decomposed in contact with a little water ; at 25° about 85 per cent. is decomposed in agreement with the symbols : $KCl.MgCl_2.6H_2O+7{\cdot}8H_2O=0{\cdot}84KCl+(MgCl_2, 0{\cdot}16KCl, 13{\cdot}8H_2O)$, where the bracketed term represents the composition of the soln. At temp. below −21°, carnallite cannot exist in contact with its soln., for it forms potassium chloride and dodecahydrated magnesium chloride ; at that temp. there is a reversible reaction $KCl+MgCl_2.12H_2O \rightleftharpoons KCl.MgCl_2.6H_2O+6H_2O$; the upper temp. limit for carnallite is 167·5°. This limiting temp. is reduced to 152·5° if magnesium chloride be present. The solubility curve AB of mixtures of $MgCl_2.12H_2O$ and KCl, is shown diagrammatically in Fig. 17 ; it extends from the eutectic temp. up to B, −21°, the temp. at which carnallite is formed, when two solubility curves BC and BD appear—the one curve, BC, represents sat. soln. of carnallite in the presence of hydrated magnesium chloride—the particular hydrate depending on the temp. ; the other curve, BD, sat. soln. of carnallite in the presence of potassium chloride. The curve BC ends at C, 152·5°, the upper limiting temp. for the existence of carnallite in the presence of magnesium chloride —at this temp., $MgCl_2.4H_2O$; while the curve BD ends at D, 167·5°, where the sat. soln. has magnesium chloride and water in the same proportion as carnallite. The curve DC represents sat. soln. of carnallite and potassium chloride with less and less water than is represented by the formula of carnallite. These three curves enclose a region BCD within which carnallite can exist in contact with the soln. indicated. The equilibrium conditions of potassium and magnesium chloride are more precisely indicated by the diagram in connection with the chapter on the Stassfurt deposits (*vide* potassium).

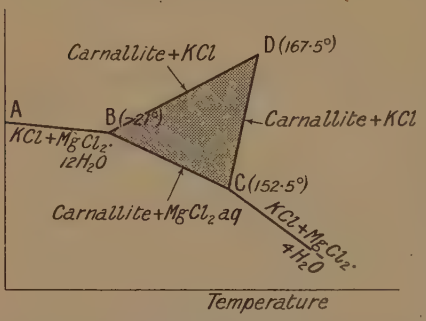


FIG. 17.—Diagrammatic Representation of the Region of Existence of Carnallite.

W. Feit and K. Kubierschky,[20] and H. Erdmann, crystallized *rubidium carnallite*, or **rubidium magnesium chloride,** $RbCl.MgCl_2.6H_2O$, from a mixed conc. soln. of the constituent salts, and measured the mutual solubility of rubidium and magnesium chlorides. Unlike carnallite, rubidium carnallite is decomposed neither by cold nor by hot water. H. L. Wells and G. F. Campbell also prepared colourless rectangular plates or flat prisms of *cæsium carnallite*, or **cæsium magnesium chloride,** $CsCl.MgCl_2.6H_2O$, by crystallization from soln. of its component salts. Double salts of a different composition were not obtained by varying the proportions of the component salts. O. Menge found that magnesium chloride forms a simple eutectiferous series with cuprous or silver chloride, Figs. 15 and 16, and from E. Chauvenet, P. Job, and G. Urbain's examination of the thermal effects attending the admixture of soln., they inferred that the double salts **cupric trimagnesium decachloride,** $2CuCl_2.3MgCl_2$, and **cupric dimagnesium decachloride,** $3CuCl_2.2MgCl_2$, exist in soln.

According to O. Menge, mixtures of calcium and magnesium chlorides furnish a simple V-eutectic at 621° and 42·8 per cent. of calcium chloride. Solid soln. appear at the calcium chloride end of the series. C. Sandonnini [21] observed no solid soln. with mixtures of strontium and magnesium chlorides, but there is a eutectic at 535°, and 50 molar per cent. of strontium chloride. With mixtures of magnesium and barium chlorides, there is a eutectic at 556° and 36 molar per cent. of barium chloride ; and with greater proportions of the latter salt, there is an arrest in the cooling curve at 590°, and at the eutectic, 556° ; only the upper arrest occurs with more barium chloride, and when still more is added the upper arrest is lowered

down to that of the eutectic. This phenomenon is taken to indicate the production of a compound of barium and magnesium chlorides which decomposes on fusion.

In 1856, C. F. Rammelsberg found a mineral in the Stassfurt salts whose analysis corresponded with **calcium dimagnesium chloride,** $CaCl_2.2MgCl_2.12H_2O$, or $Ca(MgCl_3)_2.12H_2O$, and he named it *tachhydrite*, and afterwards (1860) abbreviated it to tachydrite—from ταχύς, rapid ; ὕδωρ, water—in reference to its great hygroscopicity. The relation of tachydrite to carnallite is evident by doubling the formula of the latter ; thus, carnallite, $K_2(MgCl_3)_2.12H_2O$; tachydrite, $Ca(MgCl_3)_2.12H_2O$, where the two univalent atoms of potassium replace the bivalent atom of calcium. A. de Schulten made artificial crystals of this salt by concentrating a mixed aq. soln. of 200 grms. of anhydrous calcium chloride and 150 grms. of hexahydrated magnesium chloride on a water-bath until the liquid crystallized on cooling. A. des Cloizeaux showed that the crystals are rhombohedral (hexagonal) ; and, according to P. Groth, they have the axial ratio $a : c = 1 : 1{\cdot}900$. F. Bischof's value for the sp. gr. is 1·671 ; E. Erdmann's, 1·867 ; and J. H. van't Hoff's value is 1·6655, the mean of 1·6634 and 1·6683. R. Görgey, and H. E. Boeke give the hardness 1 to 2—that of gypsum. A. des Cloizeaux says the double refraction is negative, and the mean refractive index, according to R. Görgey, is 1·52. The salt is soluble in water—100 parts of water at 18·75° dissolve 160·3 parts of the salt. J. H. van't Hoff found the mol. ht. of soln. to be 23·55 Cals., and in the formation of a gram of tachydrite 33·82 Cals. are absorbed. F. Bischof found the temp. rises from 18·75° to 26·5° when 20 parts of tachydrite are dissolved in 80 of water.

The conditions of equilibrium have been largely determined by J. H. van't Hoff and his co-workers.[22] Below 22° a soln. of tachydrite decomposes into its component salts, so A. de Schulten's soln. furnishes tachydrite, provided the temp. is over 22°. At this temp. there is the balanced reaction : $CaCl_2.6H_2O + 2(MgCl_2.6H_2O) = CaCl_2.2MgCl_2.12H_2O + 6H_2O$. The temp. of formation is raised 0·017° per atm. increase of press. At temp. exceeding 168° tachydrite partially melts and decomposes. The conditions of equilibrium are represented graphically by J. H. van't Hoff's diagram, Fig. 18. The curve *CA* is the sat. curve of $CaCl_2.6H_2O$ and $MgCl_2.6H_2O$; *C* is at 16·7° ; *A*, the formation temp. of tachydrite, is at 21·95°. The curve *AN* is the sat. curve of $MgCl_2.6H_2O$ and tachydrite ; the curve ends at *N*, the transformation temp. of $MgCl_2.4H_2O$. The curve *AB* likewise represents the sat. curve of $CaCl_2.6H_2O$ and tachydrite ; and *BM*, of $CaCl_2.4H_2O$ and tachydrite ; *B*, 25° is the transformation temp. of $CaCl_2.6H_2O$ into $CaCl_2.4H_2O$. The curve *BG* is the sat. curve of $CaCl_2.6H_2O$ and $CaCl_2.4H_2O$; the curve *HI* is the sat. curve of magnesium chloride alone—*H*=16·7°, *I*=32° ; the curve *KG* and *GL* represents the sat. curve of calcium chloride alone, and at *G*, 29·44°, $CaCl_2.6H_2O$ passes into $CaCl_2.4H_2O$. The region *MBAN* is sat. with tachydrite ; *LGBM*, with $CaCl_2.4H_2O$; *HCANI*, with $MgCl_2.6H_2O$; and *KCABG*, with $CaCl_2.6H_2O$. Lines represent soln. sat. by the salts indicated by the adjoining regions ; and points represent soln. sat. by the salts of the adjacent regions. The

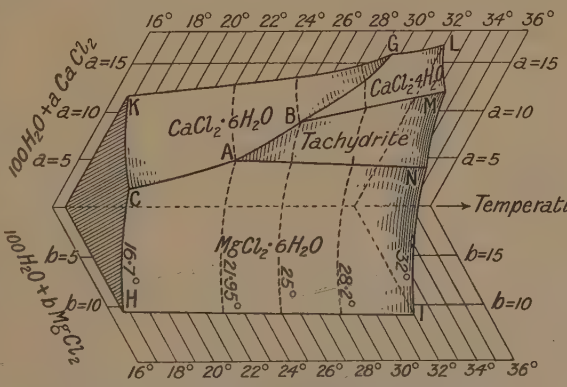


FIG. 18.—Equilibrium Curves for the System $CaCl_2$—$MgCl_2$—H_2O, after J. H. van't Hoff.

temp., 116·67°, of the transformation of $MgCl_2.6H_2O$ into $MgCl_2.4H_2O$ is not much affected by the presence of tachydrite, but the temp. of the transformation of $CaCl_2.6H_2O$ into $CaCl_2.4H_2O$ is lowered by the presence of tachydrite from 29·2° to 25°. The ternary system $MgCl_2$—$CaCl_2$—H_2O at 25° was studied by W. B. Lee and A. C. Egerton. J. Valentin obtained **potassium barium tetrachloride,** $2KCl.BaCl_2$, on the f.p. curve; and studied the ternary system $BaCl_2$—KCl—$MgCl_2$.

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§ 9. Magnesium Bromide

Magnesium bromide occurs in soln. in sea-water and brine springs. It has been reported in the Stassfurt salts, and A. J. Balard [1] extracted magnesium bromide from sea-water in 1826, and from kelp salts. The waters of the Dead Sea are particularly rich in magnesium bromide.

Bromine water slowly attacks magnesium with the evolution of hydrogen, but, according to J. A. Wanklyn and E. T. Chapman, dry liquid bromine had no perceptible action on magnesium after a year's contact. Magnesium burns in bromine vapour forming magnesium bromide, but, says R. Bunsen, the combustion is not so vigorous as in chlorine. O. Lerch conducted bromine vapour over magnesium at a red heat, when the mass became incandescent; and if any metal remained unattacked it floated as small spheres on the surface of the specifically heavier bromide. H. Gautier and G. Charpy also made magnesium bromide by direct combination of the elements. C. Löwig, and G. S. Sérullas say that a part of the magnesium bromide is carried forward by the stream of bromine vapour mixed with carbon monoxide. C. F. Rammelsberg neutralized hydrobromic acid with magnesium oxide; F. Klein neutralized the acid liquid obtained from bromine water and phosphorus by magnesia alba; and O. Lerch treated magnesium and water with liquid bromine. The evaporation of the resulting soln. furnishes crystals of hexahydrated magnesium bromide, $MgBr_2.6H_2O$. If the aq. soln. of magnesium bromide be mixed with ammonium bromide, and then evaporated to dryness, the resulting ammonium magnesium bromide gives anhydrous magnesium bromide when heated until the ammonium bromide is all expelled; otherwise, some hydrogen bromide escapes during the dehydration. O. Lerch also heated a mixture of the crystalline salt with ammonium bromide so as to prevent hydrolytic dissociation.

Anhydrous magnesium bromide, said G. S. Sérullas,[2] is a white crystalline non-volatile substance whose **crystals,** according to O. Lerch, resemble those of magnesium chloride. G. F. Hüttig gave 3·722 at 25°/4° for the **specific gravity** of anhydrous magnesium bromide, and W. Biltz, the mol. vol. as 49·48; and for the sp. gr., 3·72 at 25°/4°. The **melting point,** according to T. Carnelley, is 695°. W. Hampe found the molten mass to be a good conductor of electricity. M. Berthelot's value for the **heat of formation** is (Mg, Br_2) 140 Cals. nearly; and N. N. Beketoff's,

121·7 Cals.; J. Thomsen's value for (Mg, Br_2, aq.) is 160·5 Cals.; and N. N. Beketoff's value for ($MgBr_2$, aq.) 43·3 Cals.

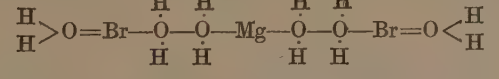
According to O. Lerch, magnesium bromide is not decomposed when heated to its m.p. provided air be excluded, but if oxygen be present, bromine is evolved and magnesium oxide is formed. When the solid or a conc. soln. is treated with conc. sulphuric acid, bromine is evolved, and, added C. Löwig, if a dil. soln. be distilled with sulphuric acid, hydrobromic acid is formed. O. Lerch said that anhydrous magnesium bromide deliquesces in air more rapidly than magnesium bromide, and that it dissolves in water with a hissing noise.

The **solubility** determinations of magnesium bromide have been made by B. N. Menschutkin,[3] A. Étard, F. Mylius and R. Funk, and I. Panfiloff. A. Étard's results are considered to be too high, and where his data cross with those of F. Mylius and R. Funk, there is a difference of 7 to 8 per cent. The data of the latter agree with those of B. N. Menschutkin, whose results, expressed in grams of $MgBr_2$ per 100 grms. of soln., are as follows:

	−10°	0°	20°	40°	60°	80°	100°	120°	140°	160°
$MgBr_2$ . . .	47·2	47·9	49·1	50·4	51·8	53·2	54·6	56·0	58·0	62·0

The solid phase over this range of temperature is **hexahydrated magnesium bromide,** $MgBr_2.6H_2O$, so that at ordinary temp. this salt crystallizes from aq. soln. The solubility of this salt is thus greater than that of the corresponding hexahydrated chloride. The equilibrium diagram has not yet been worked out. I. Panfiloff believes that at −12° there is a transition temp. below which decahydrated magnesium bromide, $MgBr_2.10H_2O$, is formed; and he obtained crystals in thin plates by cooling 45–47·8 per cent. soln. of $MgBr_2$ to −18°, and drying them below 0° by press. between filter-paper. The crystals of the decahydrated salt melt between 11·5° and 12·5° with partial decomposition: $MgBr_2.10H_2O \rightleftharpoons MgBr_2.6H_2O + 4H_2O$.

Hexahydrated magnesium bromide forms transparent prisms and needles which, according to J. H. van't Hoff and H. M. Dawson, and H. E. Boeke, are isomorphous with those of the corresponding chloride; the two salts form mixed crystals with one another. I. Panfiloff gives the **melting point** of hexahydrated magnesium bromide as 152°; B. N. Menschutkin, 164°; and F. Mylius and R. Funk, 165°. P. Bary found the salt to be fluorescent when exposed to Röntgen's or Becquerel's rays. H. Lescœur thought that his measurements of the vap. press. of the hexahydrate at different temp. corresponded with the formation of monohydrated *magnesium bromide*, $MgBr_2.H_2O$, but no other evidence is yet forthcoming of the existence of this salt. According to A. J. Balard, the crystals of hexahydrated magnesium bromide deliquesce in air, and when heated decompose into hydrogen bromide and magnesium oxide. J. L. Kreider showed, however, that approximately two of the six mols of the water may be removed from the hexahydrate between 70° and 160°, without any appreciable loss of hydrogen bromide; any further loss of water, when the salt is heated in air, is attended by a loss of hydrogen bromide—an atm. of hydrogen bromide inhibits the loss of hydrogen bromide by the salt. J. L. Kreider accordingly argued that in the molecule of hexahydrated magnesium bromide two of the six mols of water are differently placed from the other four; and he suggests the graphic formula:



There is yet no evidence of the formation of a tetrahydrated salt.

According to F. Mylius and R. Funk,[4] a soln. sat. at 18° contains 103·4 grms. of $MgBr_2$ per 100 grms. of water—*i.e.* 50·8 per cent. of $MgBr_2$, or $MgBr_2 + 9·9H_2O$—and the **specific gravity** is 1·655 (18°). For the sp. gr. of aq. soln. of magnesium bromide at 19·5°, G. T. Gerlach calculated from P. Kremers' data:

Per cent. $MgBr_2$.	5	10	15	20	30	40	50
Sp. gr. . . .	1·043	1·087	1·137	1·191	1·310	1·451	1·625

D. I. Mendeléeff also made observations on this subject. K. Jauch found the sp. ht. of soln. containing m eq. of magnesium bromide per litre, at 18°, to be

m	0·5	1·0	2·0	3·0	4·0
Sp. ht.	0·9441	0·8941	0·8068	0·7333	0·6688

H. C. Jones and F. H. Getman have investigated the **lowering of the freezing points** of soln.; while H. C. Jones and H. P. Basset have investigated the formation of hydrates in soln. from the lowering of the f.p., and the **electrical conductivities.** P. Walden measured the **equivalent conductivities** of aq. soln. H. C. Jones and co-workers found the mol conductivity, μ, and the percentage **degree of ionization,** α, of a soln. containing a mol of the salt in v litres, to be

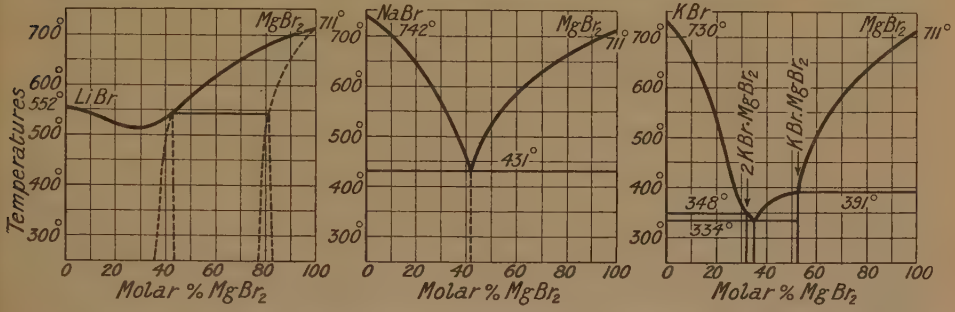
v	2	8	32	128	512	2048
$\mu_{0°}$	76·34	93·73	104·56	113·52	118·93	127·28
$\mu_{65°}$	—	324·4	367·7	412·8	445·5	471·3
$\alpha_{0°}$	59·3	71·6	79·9	86·8	90·9	97·3
$\alpha_{65°}$	—	68·8	78·0	87·6	94·5	100·0

They also measured the temp. coeff. of the conductivities. S. Meyer gave $-0{\cdot}449\times10^{-6}$ units per grm. or $-0{\cdot}083$ unit per mol for the **magnetic susceptibility** of anhydrous magnesium bromide.

Magnesium bromide is hydrolyzed by water in a manner analogous to magnesium chloride, and similar remarks apply to the formation of basic salts, or **magnesium oxybromides.** E. Tassilly,[5] boiled a soln. of 145 grms. of $MgBr_2.6H_2O$ in 300 c.c. of water, and added 5 grms. of magnesium oxide, prepared at a low temp., in small quantities at a time. The mixture was finally heated to about 150°, and filtered hot. In a few days, the soln., protected from the air, deposited needle-like crystals of $3MgO.MgBr_2.12H_2O$, which when heated to 120° in a stream of air, freed from carbon dioxide, gave crystals of $3MgO.MgBr_2.6H_2O$. This oxybromide is decomposed by water and alcohol.

W. Biltz and G. F. Hüttig,[6] and G. Spacu and R. Ripan prepared **magnesium hexamminobromide,** $Mg(NH_3)_6Br_2$; and they found the heat of formation and the temp. at which the dissociation press. is 100 mm. to be respectively 20·1 Cals., and 559° for **magnesium diamminobromide,** $Mg(NH_3)_2Br_2$, and 21·7 Cals., and 606° for **magnesium amminobromide,** $Mg(NH_3)Br_2$. A. de Schulten prepared rhombic prisms of **ammonium magnesium bromide,** $NH_4Br.MgBr_2.6H_2O$, or hexahydrated *ammonium tribromomagnesiate*, $NH_4MgBr_3.6H_2O$, or *ammonium bromocarnallite* isomorphous with the corresponding potassium salt, $KBr.MgBr_2.6H_2O$, by evaporating an aq. soln. of 30 grms. of ammonium bromide, and 250 grms. of hexahydrated magnesium bromide over sulphuric acid. The rhombic (pseudo-tetragonal) crystals have the axial ratio $a:b=1:1{\cdot}0255$, and sp. gr. 1·989. The same crystals were made by O. Lerch. G. Kellner studied the binary systems of magnesium bromide with lithium, sodium, and potassium bromides. The products are isomorphous with the corresponding chlorides. No case of dimorphism was observed. The results are summarized in Figs. 19 to 21. Lithium bromide forms solid soln. of limited conc. Sodium and magnesium bromides form a simple eutectiferous series with the eutectic at 431°. Potassium and magnesium bromides form double salts—potassium magnesium tetrabromide, $2KBr.MgBr_2$, and potassium magnesium tribromide, $KBr.MgBr_2$, which decompose respectively at 348° and 391°, and there is a eutectic between them at 334°. Solid soln. are not formed. A. de Schulten made crystals of **hexahydrated potassium magnesium tribromide,** or *potassium tribromo-magnesiate*, $KMgBr_3.6H_2O$, by a method similar to that employed for the ammonium salt. W. Feit first made the same salt by mixing a soln. of 12 grms. of magnesium bromide, sat. at ordinary temp. with a boiling sat. soln. of one grm. of potassium bromide. On cooling, crystals of the last-named salt separated out, but which on standing were transformed into the salt in question. On account of the analogy between this salt and carnallite, it has been called *bromocarnallite*. According to A. de Schulten, it forms transparent prisms belonging to the rhombic (pseudo-tetragonal)

system with axial ratio $a : b = 1 : 1{\cdot}0255$; the sp. gr. is 2·134 (15°). The crystals of $2KBr.MgBr_2.6H_2O$, reported by C. Löwig, could not be made by A. de Schulten, O. Lerch, or W. Feit ; they are thought to be a mixture of $KBr.MgBr_2.6H_2O$ with some potassium bromide. H. E. Boeke has constructed the equilibrium diagram of potassium and magnesium chlorides and bromides in water at 25°. The mixed crystals of carnallite and bromocarnallite appear in three different modifications : (i) those with from 0 to 12·2 mol per cent. are rhombic pseudo-hexagonal, resembling carnallite ; (ii) those with from 12·2 to 85 mols per cent. have the tetragonal form ; and (iii) those with 85 to 100 mols per cent. are rhombic pseudo-tetragonal. H. L. Wells and G. F. Campbell made crystals of **cæsium magnesium**



Figs. 19 to 21.—Freezing-point Curves of Binary Mixtures of Magnesium Bromide with Lithium, Sodium, and Potassium Bromides.

bromide, $CsBr.MgBr_2.6H_2O$, by a process similar to that used for the corresponding chloride ; the general properties of the two salts were similar.

According to B. N. Menschutkin,[7] magnesium bromide forms compounds $MgBr_2.6CH_3OH$ with methyl alcohol ; $MgBr_2.6C_2H_5OH$ with ethyl alcohol ; $MgBr_2.6C_3H_7OH$ with propyl alcohol ; $MgBr_2.6(CH_3)_2CH.CH_2OH$ with isobutyl alcohol ; and $MgBr_2.4(CH_3)_2.CHOH$ in isopropyl alcohol. Similarly, with ether it forms $MgBr_2.(C_2H_5)_2O$. He also made hexa-compounds with formic and acetic acids ; and obtained compounds of magnesium bromide with aniline—$MgBr_2.6C_6H_5NH_2$; $MgBr_2.4C_6H_5NH_2$; and $MgBr_2.2C_6H_5NH_2$ or $MgBr_2.C_6H_5NH_2$. Magnesium bromide also forms compounds with phenyl hydrazine, etc. The solubility of these salts in the corresponding solvent was also investigated, and in general, the higher the alcohol in the series the smaller the solubility of the corresponding alcoholate.

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§ 10. Magnesium Iodide

Small traces of magnesium iodide have been reported in sea-water and in certain saline waters. For example, some mineral springs in Java contain magnesium iodide eq. to 0·012 grm. per litre, and iodine can be obtained from the water by the copper sulphate process. According to R. Bunsen,[1] magnesium burns vigorously in iodine vapour, forming anhydrous magnesium iodide, MgI_2, but, according to T. L. Phipson, iodine may be distilled from magnesium without appreciable action; O. Lerch also found that magnesium does not react with iodine unless the metal is melted, and he recommends melting the metal in a vertical tube of hard glass, sealed at one end; when solid iodine is dropped on the molten metal, a vigorous reaction occurs with incandescence. Air should be excluded as much as possible or some magnesium oxide will be formed—globules of the unchanged magnesium float on the surface of the heavier iodide. F. Bodroux noted the action of iodine on magnesium in the presence of water; when water is dropped on a mixture of magnesium filings and iodine, the reaction is quite brilliant, and suited for a lecture experiment. O. Lerch made magnesium iodide by heating anhydrous magnesium chloride with ammonium iodide, when ammonium chloride volatilizes, and molten magnesium iodide remains; he obtained a similar result by heating ammonium magnesium iodide with an excess of ammonium iodide, first driving off the water at a relatively low temp. and afterwards subliming the ammonium iodide at a higher temp.

G. F. Hüttig gave 4·244 at 25°/4° for the **specific gravity** of anhydrous magnesium iodide, and W. Biltz gave 65·36 for the mol. vol. and 4·244 to 4·268 for the sp. gr. at 25°/4°. According to O. Lerch, the **melting point** of anhydrous magnesium iodide lies above that of the corresponding bromide, as does magnesium bromide above the corresponding chloride. The crystals are snow white, but they are usually coloured by iodine, because, says O. Lerch, the anhydrous iodide is decomposed at ordinary temp. by atm. oxygen; and M. Berthelot converted the iodide completely into oxide by heating it in oxygen. The anhydrous iodide dissolves in water with a hissing noise, and O. Lerch found the salt is also soluble in alcohol, ether, and methyl iodide; and W. Eidmann says the hydrated salt is soluble in acetone. B. N. Menschutkin obtained a series of compounds of magnesium iodide with methyl and ethyl alcohols, ether, the alkyl esters, and acetic acid—$MgI_2.6CH_3OH$; $MgI_2.6C_2H_5OH$; $MgI_2.2(C_2H_5)_2O$; etc.—analogous to those obtained with magnesium bromide. He also measured the solubilities of these compounds in the corresponding menstrua.

F. Faktor, and J. A. Wanklyn and E. T. Chapman noted that aq., alcoholic, and ethereal soln. of iodine act slowly on magnesium. According to I. Panfiloff,

if hydriodic acid be sat. with freshly precipitated magnesium hydroxide, at ordinary temp., crystals of the octohydrate are formed. O. Lerch found that if the soln. obtained by the joint action of iodine, water, and magnesium be decanted from the basic iodide, and slowly evaporated over sulphuric acid, the liquid becomes brown and furnishes crystals of octohydrated magnesium iodide, $MgI_2.8H_2O$. This salt melts at 41°, according to I. Panfiloff; 45°, F. Mylius and R. Funk; 43·5°, B. N. Menschutkin. It effloresces over sulphuric acid, and deliquesces in air. B. N. Menschutkin showed that hexahydrated magnesium iodide, $MgI_2.6H_2O$, is the stable form between 44° and upwards of 200°, and his data for the solubility of magnesium iodide in grms. of MgI_2 per 100 grms. of soln. are:

	0°	20°	40°	43°	50°	90°	140°	160°	200°
MgI_2	50·0	53·4	57·8	59·4	61·6	62·1	62·5	63·0	64·1
Solid phase	$MgI_2.8H_2O$			⇌	$MgI_2.6H_2O$				

The m.p. of the octohydrated salt is between 43° and 43·5°; the hexahydrated salt does not melt in a sealed tube at 180°–190°, but the walls of the tube begin to get a brown film; and above 200°–210°, the salt decomposes. Consequently, the anhydrous iodide is not made by the dehydration of the hydrated salt. A comparison of the solubility curves of the three hexahydrated salts—$MgCl_2.6H_2O$; $MgBr_2.6H_2O$; and $MgI_2.6H_2O$—shows that in passing from the chloride to the iodide, as is frequently the case with the metal halides, the solubility increases. If an aq. soln. of a mol of MgI_2 in 10 mols of water be cooled to 8°, colourless six-sided crystalline plates of decahydrated magnesium iodide, $MgI_2.10H_2O$, are formed which, after drying between filter paper at −4° to −5°, melt at 23°.

According to F. Mylius and R. Funk, a soln. sat. at 18° has a sp. gr. 1·909, and contains 59·7 per cent. of MgI_2 or 148 grms. of MgI_2 per 100 grms. of water. According to G. T. Gerlach, P. Kremers' data give for the sp. gr. of soln. at 19·5°:

Per cent. MgI_2	5	10	20	30	40	50	60
Sp. gr.	1·043	1·088	1·194	1·32	1·474	1·668	1·915

According to A. Heydweiller, the eq. electrical conductivity with 4, 0·5, and 0·05 gram-eq. per litre at 18° rises from 41·0 to 75·7, and to 94·6 respectively. Data for the **transport numbers** of the ions of magnesium iodide were obtained by W. Hittorf.

F. Ephraim,[2] and W. Biltz and G. F. Hüttig prepared **magnesium hexammino-iodide,** $Mg(NH_3)_6I_2$; and W. Biltz and G. F. Hüttig found that with **magnesium diammino-iodide,** $Mg(NH_3)_2I_2$, the heat of formation is 22·7 Cals.; and at 636°, the dissociation press. is 100 mm. O. Lerch, and A. de Schulten evaporated a soln. of 15 grms. of ammonium iodide and 125 grms. of hexahydrated magnesium iodide in vacuo over sulphuric acid, and obtained hygroscopic prismatic crystals of **ammonium magnesium iodide,** $NH_4I.MgI_2.6H_2O$. G. Spacu made complex salts of magnesium iodide with triethylenediammine and diethylenediammine. The corresponding **potassium magnesium iodide,** $KI.MgI_2.6H_2O$, was similar, and was prepared in a similar manner. The sp. gr. of the former was 2·346 (15°) and of the latter 2·547 (15°). The potassium salt has been called *iodocarnallite*, and the ammonium salt *iodo-ammonium carnallite*. H. E. Boeke found that carnallite does not form mixed crystals with iodocarnallite. **Magnesium iodo-chloride,** $MgCl_2.2ICl_3.8H_2O$, was made by E. Filhol by triturating conc. hydrochloric acid with magnesium iodate, and by saturating an aq. soln. of magnesium iodide with chlorine, or mixing iodine trichloride with magnesium chloride; and R. F. Weinland and F. Schlegelmilch, by the action of chlorine on a mixture of iodine and magnesium chloride in water. It forms yellow deliquescent needle-like crystals which resemble the potassium analogue: $KICl_4$ or $KCl.ICl_3$. C. K. Tinkler obtained some evidence of the existence of *magnesium polyiodide* from the identity of the absorption spectra of soln. of magnesium iodide and iodine with the spectra of analogous soln. of cadmium, sodium, potassium, barium, zinc, and aluminium.

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§ 11. Magnesium Sulphides

L. Kessler [1] made **magnesium sulphide,** MgS, by the action of hydrogen sulphide on red-hot magnesia, by heating a mixture of magnesium and sulphur, and by plunging burning magnesium in a jar of dry hydrogen sulphide; but F. G. Reichel found that magnesium does not readily combine with molten sulphur, although a little is formed if the sulphur be heated with carbon, or if the two elements be heated in a stream of hydrogen or hydrogen sulphide, and A. Mourlot also obtained the sulphide by heating a mixture of sulphur and magnesium filings in hydrogen; F. G. Reichel, and J. Parkinson, by passing the vapour of sulphur mixed with hydrogen over the red-hot metal. E. Tiede could not get magnesium sulphide prepared by this process free from magnesium by the sublimation of the metal in vacuo; but a highly purified product was obtained by boiling for 3 hrs. in a reflux condenser 10 grms. of the crude sulphide with 100 c.c. of ether freshly distilled from sodium, 10 grms. of ethyl iodide, and a fragment of iodine. Moisture must be excluded. The residue was washed with ether, and dried in a vacuum desiccator on a water-bath. E. Tiede and F. Richter made the anhydrous sulphide by heating the oxide in a current of nitrogen laden with the vapour of carbon disulphide. O. Schumann found very little magnesium sulphide is produced by passing hydrogen sulphide over red-hot magnesium oxide, but A. Mourlot observed a slow transformation by heating the oxide or sulphate at about 1200° in a stream of hydrogen sulphide. E. Tiede had no success by heating anhydrous magnesium sulphate for an hour at 1200° in a stream of hydrogen sulphide, although at 450° water and sulphur were formed. F. Briegleb and A. Geuther obtained the sulphide by the action of the same gas on magnesium nitride. E. Frémy prepared the sulphide mixed with a little polysulphide by passing the vapour of carbon disulphide over red-hot magnesium oxide, and F. G. Reichel found that some carbonyl sulphide is formed at the same time: $MgO+CS_2=MgS+COS$, and if the vapour of carbon disulphide is mixed with carbon dioxide, some **magnesium oxysulphide,** MgO.MgS, is formed. According to A. Mourlot, the amorphous sulphide obtained by these methods is converted into the crystalline state by heating it for a few minutes in an electric arc-furnace; and he also obtained crystalline magnesium sulphide by heating a mixture of magnesium chloride and stannous sulphide in the electric arc-furnace. Magnesium sulphide is not obtained by heating the sulphate with carbon, hydrogen, hydrogen sulphide, ammonium sulphide or carbon monoxide. P. Berthier obtained but a small conversion of magnesium sulphate to sulphide by heating the sulphate with carbon, and A. Mourlot said that the conversion is incomplete in the electric arc-furnace.

The colour of the amorphous magnesium sulphide so far prepared varies from pale red to reddish-brown. E. Tiede's sample was reddish-white and amorphous. A. Mourlot stated that the **crystals** belonged to the cubic system According to W. L. Bragg, the **X-radiogram** corresponds with a simple cubic lattice with the neighbouring atoms 2·54 A. apart. S. Holgersson gave 5·078±0·012 A. The crystalline sulphide has a **specific gravity** 2·79–2·85 at 15°, while the amorphous sulphide has a sp. gr. 2·2 at 15°. P. Sabatier's value for the **heat of formation** (Mg, S_{solid})=79·6 Cals., and the heat of the reaction : ($MgS, HCl_{dil.\ aq.}$)=21·80 Cals. at 13°. E. Tiede prepared a sample free from spectroscopic traces of alkaline earths, and from organic solvents, and when exposed for a few seconds to daylight or arc-light, it became faintly luminous. Less purified samples were more **phosphorescent.** Pure magnesium sulphide, say E. Tiede and F. Richter, is not phosphorescent, but it becomes so by suitable additions of manganese, bismuth, or antimony ; the optimum amounts per gram of sulphide are 0·001–0·002 grm. of manganese chloride or sulphate ; 0·0024 grm. of basic bismuth nitrate ; or 0·0013 grm. of potassium antimonyl tartrate. E. Tiede and A. Schleede discussed the preparation and properties of phosphorescent magnesium sulphide. Magnesium sulphide is more sensitive to the rays of long wave-length. No excitation was observed with **X-rays, radium rays,** or **ultra-violet light ;** but in the **cathode rays,** it gives a lively blue and red fluorescence, with a feeble after-glow.

The amorphous sulphide prepared by F. G. Reichel, and J. Parkinson developed hydrogen sulphide when exposed to moist **air,** and in contact with cold **water,** magnesium hydrosulphide, $Mg(SH)_2$, is formed. According to E. Frémy, water dissolves magnesium sulphide very sparingly, and on standing hydrogen sulphide is evolved and magnesium hydroxide is precipitated ; the action is rapid with warm water. According to A. Mourlot, water does not attack the crystalline sulphide in the cold, but when heated, magnesium oxide and hydrogen sulphide are formed. O. Schumann found that in superheated steam, magnesium sulphide is decomposed, furnishing hydrogen sulphide, sulphur, sulphur dioxide, and magnesium oxide. Magnesium sulphide is not changed by heating it in **hydrogen, coal gas,** or **carbon monoxide,** but if any polysulphide is present, the excess of sulphur was found by F. G. Reichel to be withdrawn.

According to A. Mourlot, **chlorine** reacts with crystalline magnesium sulphide at 300°, and the mass becomes incandescent with the formation of sulphur chloride and magnesium chloride ; **bromine** and **iodine** act at dull redness in a similar way without incandescence. The crystalline sulphide is decomposed in the cold by **hydrogen fluoride** and **hydrogen chloride ;** if warm, the mass becomes red hot. The **metalloid chlorides** react with the suitably heated crystalline sulphide, forming the corresponding oxide—the reaction is quite vigorous with **phosphorus trichloride** or with **arsenic trichloride**—**chromyl chloride** behaves similarly. The action of **oxygen** on the warm crystalline sulphide is quite vigorous and sulphur dioxide is formed ; **oxidizing agents** also react vigorously with crystalline magnesium sulphide—even **phosphorus pentoxide** is reduced to phosphorus sulphide. F. G. Reichel found that when the vapour of **sulphur** mixed with hydrogen or hydrogen sulphide is passed over amorphous magnesium sulphide, no polysulphide is formed, nor does **carbon disulphide** unite with the sulphide. A. Mourlot found dil. or conc. **sulphuric acid** reacts with crystalline magnesium sulphide with the evolution of hydrogen sulphide ; and with cold conc. **nitric acid,** sulphur is separated. The crystalline sulphide is not reduced by **phosphorus** at 1000°, and at a red heat, **boron** and **silicon** have no action. The crystalline sulphide is not reduced by **carbon** when heated for 15 mins. in the electric-arc furnace, no carbide is formed, and no volatilization is perceptible. H. C. Geelmuyden found that **calcium carbide** reduces magnesium sulphide in the electric-arc furnace, and the metal is volatilized. Crystalline magnesium sulphide is reduced by **sodium** without incandescence ; but **iron** does not reduce it at a dull red heat. F. G. Reichel also found that if the amorphous sulphide is heated with iron or with **copper,** the

corresponding sulphide is formed, but he did not succeed in isolating magnesium. T. Petitjean has also studied these reactions.

V. Calcagni found 100 c.c. of a cold sat. soln. of magnesium hydroxide dissolved 0·014 grms of sulphur so that the relation is Mg : S = 1 : 2. The soln. responds to the reactions for sulphides, polysulphides, thiosulphates, and sulphites. According to F. G. Reichel, if magnesium sulphide be warmed with water and sulphur, not to the b.p., a dark yellow liquid is produced which presumably contains **magnesium polysulphide**. This liquid decomposes when exposed to the air, and gives off hydrogen sulphide, forming sulphur, magnesium hydroxide, and a trace of magnesium thiosulphate. The liquid is slowly decomposed when boiled, but more slowly than magnesium sulphide. The sulphides of antimony and arsenic dissolve in the liquid, but not so with the sulphide of mercury. J. Stingl and T. Morawsky prepared **magnesium trisulphide**, Mg_4S_3, by the action of magnesium chloride on calcium polysulphide.

F. G. Reichel found that with cold water, amorphous magnesium sulphide furnishes **magnesium hydrosulphide**, $Mg(SH)_2$, thus : $2MgS+2H_2O=Mg(OH)_2+Mg(SH)_2$. According to J. J. Berzelius, and T. J. Pelouze finely divided magnesium hydroxide suspended in water is slowly but abundantly dissolved when hydrogen sulphide is passed through the liquid, and a soln. of magnesium hydrosulphide is formed. A. Béchamp, and L. Naudin and F. de Montholon, used magnesium carbonate ; and E. Divers and T. Shimidzu prepared a soln. by suspending one part of freshly calcined magnesia in not less than ten parts of water. A stream of hydrogen sulphide is passed through the liquid, and the magnesia slowly passes into soln., although much gas passes away unabsorbed. If much more magnesia be added to the water, the resulting soln. of magnesium sulphide is not so conc. as if the proportion of magnesia be less. The soln. can be preserved unchanged by corking the flask and sealing the cork with wax or paraffin to exclude air ; when exposed to air, an alkaline liquid is formed which contains magnesium acid carbonate as well as magnesium hydroxide. Magnesium hydrosulphide mixed with an alkali salt is obtained by mixing a soln. of a magnesium salt with an alkali hydrosulphide or barium hydrosulphide. F. Gerhard prepared a similar soln. by mixing magnesium sulphate with sodium sulphide or calcium sulphide ; J. Thomsen, and A. Béchamp worked with a soln. of barium hydrosulphide.

J. J. Berzelius, and A. Béchamp, found that the soln. decomposes when an attempt is made to conc. it by evaporation in vacuo or in an atm. of hydrogen ; F. G. Reichel found some thiosulphate is formed. Similarly, when the soln. of magnesium hydrosulphide is mixed with a conc. soln. of potassium hydrosulphide, or when a conc. aq. soln. of magnesium chloride is mixed with a conc. soln. of potassium hydrosulphide, hydrogen sulphide is given off. The soln. is also decomposed on boiling. According to E. Divers and T. Shimidzu, when the impurities have settled, the soln. is nearly colourless, and the slight yellow coloration is due to polysulphide formed by the action of ferric oxide in the magnesia, or of air. The polysulphide is decomposed by hydrogen sulphide and sulphur when the products are magnesium hydrosulphide and sulphur ; and it is but slightly decomposed by boiling the liquid when the products are magnesium hydroxide, sulphur, and hydrogen sulphide. At 12°, a soln. of magnesium hydrosulphide with 16·31 per cent. of $Mg(SH)_2$ has a sp. gr. 1·118 ; the aq. soln., at 60°, develops a steady stream of hydrogen sulphide, and magnesium hydroxide is precipitated, and the evolution of gas can be maintained for a considerable time longer by raising the temp. to 90°–100°. This is recommended by them as a source of arsenic-free hydrogen sulphide. The aq. soln. oxidizes on exposure to air, forming thiosulphate and polysulphide. "If the soln. be left at rest, oxidation is much impeded by the formation of a firm colourless transparent amorphous film on the surface of the liquid, consisting apparently of magnesium hydroxide, but possibly of *magnesium hydroxyhydrosulphide*, Mg(OH)SH. The soln. does not readily, if at all, absorb carbon dioxide from the atm. in the early stages of its decomposition." Magnesium hydrosulphide is readily decomposed by an acid giving off hydrogen sulphide. A soln. of magnesium hydrosulphide dissolves antimonic or mercuric sulphide, forming

thiosalts. J. Thomsen found for the heat of formation, (Mg, 2S, H_2)aq.=114·88 Cals., and ($MgO_{aq.}$, $2H_2S_{aq.}$)=15·68 Cals.

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§ 12. Magnesium Sulphates

Magnesium sulphate occurs in nature in rhombic crystals of *kieserite* or *reichardite*, which is the monohydrated sulphate, $MgSO_4.H_2O$. The mineral may be massive, compact, or granular. Early analyses were made by C. F. Rammelsberg, M. Siewert, B. Leopold, L. N. Vauquelin, and E. Reichardt.[1] It occurs in the Stassfurt salt-mines in beds 9–12 ft. thick with alternating layers of sodium chloride; and it is often mixed with carnallite and gypsum. Magnesium sulphate also occurs in rhombic crystals as *Epsom salts*, or *epsomite*, which is the heptahydrated sulphate, $MgSO_4.7H_2O$. Heptahydrated magnesium sulphate has received many other names: *Seidlitz salt, sal amarum, sal anglicum, sal cathartícum, Seidschütz salt, bitter salts*, etc. The mineral appears as a delicate fibrous scum or efflorescence on walls, and rocks; and in the galleries of mines and caves; it has been reported in gypsum mines, limestone caves, and on dolomites, serpentines, etc. W. H. Emory [2] reported it in the Californian plains, east of San Diego. Magnesium sulphate is also found in many mineral waters and springs, and in the bittern of sea-water. Analyses have been made by J. Bouis, A. Dufrénoy, F. Stromeyer and J. F. L. Hausmann, etc. It also occurs combined with calcium, sodium, and potassium sulphates as complex or double salts (*q.v.*).

Crude salts are mined, and shipped as a commercial grade, or the salts may be refined by crystallization. Magnesium sulphate obtained by crystallization from aq. soln. is usually in the form of epsomite, *i.e.* the heptahydrate; and it is conveniently made by dissolving the oxide, hydroxide, or carbonate in sulphuric acid, and evaporating the soln. to crystallization. The purified carbonate or hydroxide can be obtained from the purified chloride, *q.v.* It is doubtful if crystals of the anhydrous sulphate have been made. According to T. Graham,[3] anhydrous magnesium sulphate, $MgSO_4$, is obtained by heating the hydrated salt "to an incipient red heat for a considerable time." Incipient red heat is certainly over 500°. Hence, from G. H. Bailey's observations some oxide is probably formed as well. C. Schmidt made the anhydrous sulphate by warming the heptahydrate to 200°. H. G. F. Schröder found all the water is expelled from the hydrated salt in vacuo at 180°.

Magnesium sulphate has been obtained by evaporation from mineral waters and salt springs; or as a by-product from the mother liquid remaining after the evaporation of sea-water in making sea-salt. F. Michels [4] prepared it from the kieserite remaining after the extraction of potassium chloride from the Stassfurt Abraumsalzen. E. F. Anthon obtained it as a by-product in the preparation of carbon dioxide by the action of sulphuric acid on magnesite. J. H. Swindells treated dolomite with sulphuric acid, but found much

acid was expended in converting the calcium carbonate into sulphate; and F. Findeisen proposed to remove the lime by washing calcined dolomite with water—*vide* the decalcification of dolomite. The impurities in commercial magnesium sulphate have been discussed by W. L. Kölreuter,[5] J. S. F. Pagenstecher, and by E. Biltz, and E. Merck.

The hydrates of magnesium sulphate.—Hydrates of magnesium sulphate, $MgSO_4.nH_2O$, have been reported, with n=1, 1·5, 2, 4, 5, 6, 7, and 12. The hexa- and hepta-hydrates have each two different crystalline forms. The mineral *kieserite* occurring in the Stassfurt salt-beds, Hallstadt, etc., and named after M. Kieser, of Jena, is the native form of **monohydrated magnesium sulphate,** $MgSO_4.H_2O$. This is a light grey, fine-grained mass which has been analysed by C. F. Rammelsberg,[6] E. Reichardt, J. Bräuning, etc. According to H. Grüneberg, the grains are often cemented together with sodium chloride, which can be removed by washing. L. Playfair and J. P. Joule made the monohydrate by heating the heptahydrate to 130°–140°. According to J. H. van't Hoff, W. Meyerhoffer, and N. Smith, it is formed by heating the heptahydrate to 132°; its temp. of formation from the hexahydrate is between 67° and 68°, so that the intermediate hydrates can be formed only by slowing down the speed of the transformation. Well-formed crystals are not common; but it does occur as octahedral crystals. According to G. Tschermak, the crystals do not lose their water at 100°, and when heated to a higher temp., they fly to pieces without melting. G. Clemm found that the crystals dissolve unchanged in cold water, and that the solubility does not exceed that of gypsum. The solubility curve is indicated in connection with Fig. 22. When kept in moist air, E. Reichardt found that the crystals become opaque, take up a mol of water, and set like a cement; while F. Bischof said that under water, the crystals likewise set to a cement-like mass which dissolves in warm water as the heptahydrate. According to H. Grüneberg, when the crystals are calcined—presumably the anhydrous salt is formed—the powdered mass readily dissolves in hot water. T. Graham showed that the odd mol of water is not expelled from the monohydrate at 210°–238°, and he applied the term *water of constitution* or *water of halhydration* to this mol of water to distinguish it from the water of crystallization. S. U. Pickering said that the gist of this theory is that the so-called constitutional water is not *water* at all, but hydrogen and oxygen, forming part of the salt nucleus itself; crystallized magnesium sulphate is not the heptahydrate of $SO_2(MgO_2)$ but the hexahydrate of $SO(MgO_2)(HO)_2$, that this latter salt (improperly regarded as a monohydrate, $SO_2(MgO_2).H_2O$, is an "atomic" compound decomposable by heat into $SO_2(MgO_2)+H_2O$, just as monosodium phosphate, $PO(NaO)(HO)_2$, is decomposed by the same agent into a totally different salt, $PO_2(NaO)$ and H_2O. He further argued that we have no grounds for supposing that the various water mols. in a hydrated salt are not all combined in a similar manner, and do not all occupy exactly the same position with regard to the salt nucleus; that, in short, a hydrated salt is not a symmetrical substance. At the same time, it must be admitted that we have no positive evidence to show that it is symmetrical. E. Erlenmeyer represented the formula of magnesium sulphate with a molecule of T. Graham's water of halhydration, by $HO.Mg.HSO_4$.

Analyses by C. F. Rammelsberg, and by E. Reichardt point to the possible existence of a hydrate intermediate between the mono- and di-hydrates; N. A. E. Millon also obtained a hydrate which he regarded as $MgSO_4.1\frac{1}{2}H_2O$, by heating a higher hydrate to 110°–115° while the monohydrate is formed at 140° to 180°; J. H. van't Hoff and H. M. Dawson showed that the composition more probably corresponds with **pentatetritahydrated magnesium sulphate,** $MgSO_4.1\frac{1}{4}H_2O$, and that it is best obtained by keeping the soln. used for the preparation of the tetrahydrate, or by evaporating that soln., at a rather higher temp. than is employed for the last-named salt. These temp. are above the transition temp. for the change $MgSO_4.4H_2O \rightarrow MgSO_4.1\frac{1}{4}H_2O$, which is nearly 20°, but at 20° the evaporation must be very slow to produce the pentatetritahydrate. This salt crystallizes more readily than the dihydrate from which it is readily obtained,

in the presence of magnesium chloride, by evaporation at 65°. The crystals of this hydrate are quite different from those of kieserite.

L. Playfair prepared **dihydrated magnesium sulphate,** $MgSO_4.2H_2O$, by boiling the finely powdered heptahydrate with absolute alcohol, and also by heating the heptahydrate to 100°. Observations by N. A. E. Millon pointed to the existence of a dihydrated magnesium sulphate. J. H. van't Hoff and H. M. Dawson found that this salt is not obtained by keeping at 25° the soln. containing magnesium chloride from which the tetrahydrate is produced, but is formed by evaporating the soln. at a higher temp. when a white, badly crystallizing, mass is formed along with the crystals of the tetrahydrate. The transition temp. $MgSO_4.4H_2O \rightarrow MgSO_4.2H_2O$ is approximately 25°, and the change, at this temp., can be observed under the microscope. J. B. Hannay obtained evidence of the formation of this compound from the dehydration curve of the higher hydrates; and J. Thomsen from the heats of hydration.

According to J. H. van't Hoff and T. Estreicher-Rozbiersky, when a soln. of magnesium sulphate and chloride is evaporated over sulphuric acid at 25°, crystals of the hepta- and hexa-hydrates first separate, then follow crystals of **pentahydrated magnesium sulphate,** $MgSO_4.5H_2O$, and later still, six-sided plates of **tetrahydrated magnesium sulphate,** $MgSO_4.4H_2O$, appear. The crystals of the two last-named salts are unstable. L. Playfair, and T. E. Thorpe and J. I. Watts claimed to have made the pentahydrate by drying the heptahydrate over sulphuric acid until it ceased to lose weight. J. H. van't Hoff, W. Meyerhoffer, and N. Smith found the transition temp. $MgSO_4.5H_2O \rightarrow MgSO_4.4H_2O$, to be 77·5°; and nearly the same temp. for $MgSO_4.6H_2O \rightarrow MgSO_4.5H_2O$.

W. Haidinger, and H. Löwel obtained monoclinic crystals of **α-hexahydrated magnesium sulphate,** α-$MgSO_4.6H_2O$, resembling those of borax, by evaporating an aq. soln. of magnesium sulphate until a skin is formed, and then keeping the soln. for a long time at 25° to 30°. J. C. G. de Marignac recommended draining the crystals, and drying them at 100°. According to E. Mitscherlich, the crystals of the heptahydrate at 52° rapidly lose one-seventh of their water, and form an aggregate of small prisms. H. Löwel observed that when a soln., prepared by dissolving 200 to 225 parts of the heptahydrate in 100 parts of water, is allowed to stand for some time in a closed vessel, monoclinic crystals of the hexahydrate, or hexagonal crystals of the heptahydrate, may be formed; if the temp. is between 14° and 21°, the crystals form slowly and appear as long prisms; if the temp. be lower than this, the crystals form rapidly and appear as small needles. According to L. de Boisbaudran, tetragonal pyramidal crystals of **β-hexahydrated magnesium sulphate,** β-$MgSO_4.6H_2O$, are produced by seeding a conc. soln. of magnesium sulphate with tetragonal crystals of nickel cupric sulphate or zinc cupric sulphate. The crystals are unstable and readily pass into the α-form. E. Wiedemann found that at about 50°, the heptahydrate passes into a labile or β-hexahydrate; J. K. van der Heide placed the temp. at 48·2°, and later, 47·2°. In the presence of potassium sulphate, E. Wiedemann found that the labile β-hexahydrate passed into the stable α-form at 90°; or, according to J. K. van der Heide, at 88·5°.

The crystallization of an aq. soln. of magnesium sulphate below 25° furnishes the ordinary or rhombic crystals of **α-heptahydrated magnesium sulphate,** α-$MgSO_4.7H_2O$. This salt is represented in nature by the mineral *epsomite*. According to H. Löwel, a second form: **β-heptahydrated magnesium sulphate,** β-$MgSO_4.7H_2O$, appears in monoclinic crystals when a supersaturated aq. soln. of 200 to 225 grms. of heptahydrated magnesium sulphate is kept between 14° and 21° for some time; and L. de Boisbaudran obtained the β-heptahydrate by seeding a rather more dil. soln. with a crystal of cupric or ferrous sulphate. E. Jänecke found the heptahydrate is in equilibrium with the hexahydrate at 51°. S. Takegami obtained **octohydrated magnesium sulphate,** $MgSO_4.8H_2O$, and he gave for the transition points:

$$MgSO_4.8H_2O \overset{48\cdot2^\circ}{\rightleftharpoons} MgSO_4.7H_2O \overset{77\cdot2^\circ}{\rightleftharpoons} MgSO_4.6H_2O$$

J. Fritzsche prepared crystals of **dodecahydrated magnesium sulphate,** $MgSO_4.12H_2O$, by freezing a sat. soln. of magnesium sulphate below 0°, and slowly thawing out the ice at 0°. The crystals are opaque when prepared on a small scale, but transparent if prepared on a large scale. Above 0°, they give off water and are converted into opaque crystals of the heptahydrate, without changing their form.

The solubility of magnesium sulphate.—Some idea of the relationship between most of the different hydrates of magnesium sulphate can be gathered from the solubility curve, Fig. 22. Early determinations were made by J. L. Gay Lussac,[7] E. Tobler, E. Diacon, G. J. Mulder, C. von Hauer, and A. Gérardin. The first-named represented his results at $\theta°$, by the solubility curve $S=25{\cdot}76+0{\cdot}47816\theta$, but A. Étard showed that between 0° and 123° $S=20{\cdot}5+0{\cdot}2276\theta$ gives better results, and between 123° and 190°, $S=48{\cdot}5-0{\cdot}4403\theta$. The best representative values, compiled by R. Kremann for the stable binary system $MgSO_4$—H_2O, are illustrated by the continuous curve *ABCDELM*, Fig. 22. The ice-line, *AB*, by F. Rüdorff, and L. C. de Coppet, corresponds with a percentage solubility, according to L. C. de Coppet, of 13·9 per cent. $MgSO_4$ at —2·9°, and, according to J. H. van't Hoff, W. Meyerhoffer, and N. Smith, with a eutectic at —3·9° and 19 per cent. $MgSO_4$, *B*. The solubility curve *BC* refers to systems with the dodecahydrate, $MgSO_4.12H_2O$, at 1·8° and 21·1 per cent. $MgSO_4$. At the transition point *C*, 1·8°, both the dodeca- and the rhombic hepta-hydrates are in equilibrium. The solubility curve *CD* refers to systems with the rhombic heptahydrate as solid phase; at the transition point *D*, by J. K. van der Heide, 48° and 33 per cent. $MgSO_4$, both the rhombic heptahydrate and the hexahydrate are in equilibrium as solid phases. J. K. van der Heide gave 48°–48·5° for the transition point of the hepta- to the hexa-hydrate; and C. D. Carpenter and E. R. Jette gave 48·4°. The curve *DE* represents the solubility of hexahydrated magnesium sulphate where *E*, according to J. H. van't Hoff, W. Meyerhoffer, and N. Smith, represents the transition point—at 68° and 37 per cent. of magnesium sulphate—between the hexa- and mono-hydrates. The solubility curve *ELM* refers to the monohydrate. The percentage solubilities at the intermediate points are:

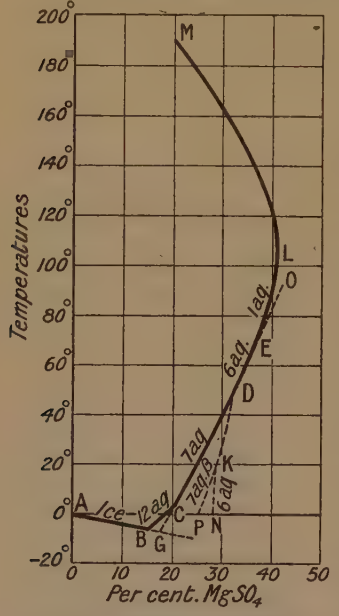

FIG. 22.—Solubility Curves of Magnesium Sulphate.

	10°	20°	30°	40°	50°	60°	80°	99·4°	164°	188°
$MgSO_4$ . .	23·6	26·2	29·0	31·3	33·5	35·5	38·6	40·6	29·3	20·3
	$MgSO_4.7H_2O$				$MgSO_4.6H_2O$		$MgSO_4.H_2O$			

where *CD* is compiled from data by H. Löwel, E. E. Basch, and G. J. Mulder; for *DE*, from G. J. Mulder; for *EL*, from A. Geiger; and for *LM*, from A. Étard. Metastable systems are represented by the continuation of the ice-line *BG* to —8·4°, a compound, according to L. C. de Coppet, with 23·6 per cent. of magnesium sulphate, and *G*, according to F. Guthrie, with the eutectic between rhombic hepta-hydrate and ice, at —5·0°, and 19 per cent. $MgSO_4$. The curve *CG* by H. Löwel represents the rhombic heptahydrate which has 20·6 per cent. $MgSO_4$ at 0°. The dotted curve *PK* by H. Löwel represents the solubility of the hexagonal hepta-hydrate with solubilities at 0°, 10°, and 20° of 25·8, 27·9, and 30·0 per cent. $MgSO_4$

respectively. The dotted curves *NK*, *KD*, and EO, by G. J. Mulder, represent the percentage solubilities of the hexahydrate :

	0°	10°	20°	30°	70°	80°	90°	100°
$MgSO_4.6H_2O$	29·0	29·7	30·8	31·2	37·3	39·1	40·8	42·5

By cooling a hot soln. of conc. *sulphuric acid* sat. with anhydrous magnesium sulphate, H. Schiff obtained a syrupy liquid which furnished six-sided plates of **magnesium hydrotetrasulphate,** $MgSO_4.3H_2SO_4$; and C. Schultz obtained crystals of **magnesium hydrodisulphate,** $MgSO_4.H_2SO_4$, or $Mg(HSO_4)_2$, under similar conditions. J. Kendall and A. W. Davidson found the solubility of normal magnesium sulphate in sulphuric acid does not exceed 1·4 molar per cent. even on boiling. The sat. temp. of soln., with the solid phase $MgSO_4.3H_2SO_4$, were :

Per cent. $MgSO_4$	0·18	0·32	0·62	0·77	1·07	1·18	1·37
Sat. temp.	25·7°	44·2°	66·0°	72·3°	82·8°	86·7°	91·7°

The salt was not completely dissolved with 1·53 per cent. $MgSO_4$. H. Haushofer found the crystals are hexagonal plates too deliquescent to be satisfactorily measured crystallographically. G. Tammann found the salt to be completely decomposed when the soln. is diluted. C. Schultz also found that boiling conc. sulphuric acid dissolves about 2 per cent. of anhydrous magnesium sulphate, and the cooling soln. deposits crystals of **magnesium hexahydrotetrasulphate,** $Mg(HSO_4)_2.2H_2SO_4$, or $MgH_6(SO_4)_4$, which K. Haushofer believed to belong to the monoclinic system.

J. B. Richter stated that magnesium sulphate dissolves much more rapidly and abundantly in dil. *hydrochloric acid* than in water, and a clear syrupy liquid is formed. According to F. Margueritte, no precipitation occurs when hydrogen chloride is passed into an aq. soln. of magnesium sulphate ; and, according to R. Schiff, no acid salt is formed. According to R. J. Kane, magnesium sulphate is not decomposed by hydrochloric acid, for it can be crystallized unchanged from its soln. in this acid. S. Setschenoff studied the absorption of *carbon dioxide* by soln. of magnesium sulphate. O. Aschan found 100 grms. of 95 per cent. *formic acid*, at 19°, dissolve 0·34 grm. of $MgSO_4$. According to C. Hensgen, anhydrous magnesium sulphate is but very sparingly soluble in conc. hydrochloric acid, and the hydrated salt dissolves therein only because its water of crystallization dilutes the acid. Hence it appears that, in the action of hydrogen chloride on the hydrated salt, the gas is at first absorbed by the water of crystallization, forming a liquid in which the anhydrous salt is soluble, but as the hydrochloric acid thus formed becomes more conc. the anhydrous sulphate is gradually deposited.

According to C. J. B. Karsten, a conc. soln. of *sodium chloride* dissolves heptahydrated magnesium sulphate without separating the former salt, but conversely, if sodium chloride be dissolved in a conc. soln. of magnesium sulphate, the last-named salt separates out. The crystallization of a soln. of the two salts re-deposits both salts in crystals without alteration, but T. F. von Grotthus found that if the residue be pulverized and boiled in alcohol, a little magnesium chloride is dissolved ; consequently, as stated by C. J. B. Karsten, the products are : magnesium chloride and sodium sulphate as well as the original salts. C. W. Scheele showed that above 0°, there is very little change, but below that temp. decahydrated sodium sulphate crystallizes out and magnesium chloride remains in soln. According to J. J. Berzelius, if a soln. of 2 parts of heptahydrated magnesium sulphate and one part of sodium chloride be dissolved in 4·5 parts of water ; evaporated a little ; and then cooled to −3°, decahydrated sodium sulphate is precipitated and magnesium chloride remains in soln. If the mixture be gently warmed the original salts are reproduced, but above 50°, added H. Rose, the soln. deposits anhydrous sodium sulphate. C. J. B. Karsten stated that an aq. soln. of magnesium sulphate is decomposed by double affinity when mixed with *ammonium chloride*, *potassium chloride*, or *potassium nitrate*, and the alkali sulphate so produced unites with the undecomposed magnesium salt to form a double sulphate. F. Pfaff found a sat.

soln. contains 13·09 parts of *sodium sulphate* and 15·31 parts of magnesium sulphate per 100 parts of water at 0°; and E. Diacon further found that 100 grms. of water dissolve at

	17·9°	24·1°	30°	33°	36°	40°
Na_2SO_4	16·70	25·70	29·73	27·82	26·29	24·01
$MgSO_4$	30·41	31·01	28·92	24·87	26·59	30·89

C. J. B. Karsten and others have also discussed this subject in connection with the double salts of magnesium sulphate with sodium or potassium sulphate. C. J. B. Karsten found heptahydrated magnesium sulphate dissolves rapidly and without precipitation in a conc. soln. of potassium nitrate, but when potassium nitrate is slowly dissolved in a conc. soln. of magnesium sulphate, potassium sulphate is precipitated. The heptahydrate dissolves in a conc. soln. of *sodium nitrate* without precipitation, but only a little sodium nitrate can be dissolved in a conc. soln. of the heptahydrate without the soln. becoming turbid owing to the separation of magnesium sulphate. H. Precht and B. Wittgen, C. J. B. Karsten, G. J. Mulder, E. Tobler, H. Schiff, and H. Schwarz made observations on the solubility of magnesium sulphate in soln. of *potassium sulphate*. H. S. van Klooster measured the percentage solubility (grams of salt in 100 grms. of sat. soln.) of magnesium sulphate in aq. soln. of potassium sulphate, and found :

$MgSO_4$	26·76	26·57	26·39	16·36	13·26	12·68	10·69	4·00	0
K_2SO_4	0	2·34	4·02	8·43	10·34	10·70	10·84	11·03	10·77
Solid phases	$MgSO_4.7H_2O$		$MgSO_4.K_2SO_4.6H_2O$				K_2SO_4		

According to C. J. B. Karsten, an aq. soln. of magnesium sulphate dissolves some **calcium hydroxide** from which calcium sulphate and magnesium hydroxide separate when the soln. is dil., and a basic magnesium sulphate if the soln. is conc. According to H. Grüneberg, a mixture of 2 mols of kieserite, and one of calcium hydroxide made into a slip with water, sets to a hardness with the evolution of heat; if the mixture be calcined and powdered, and again mixed with water, a marble-like mass is formed. C. J. B. Karsten found a soln. of magnesium sulphate dissolves a little **calcium sulphate,** while J. H. Dröze found that a conc. soln. of magnesium sulphate dissolves no calcium sulphate, and gypsum is precipitated from its aq. soln. by adding some heptahydrated magnesium sulphate; according to R. Fassbender, the precipitate contains 15 per cent. of magnesium sulphate and has a crystalline form different from gypsum. T. S. Hunt and F. Hoppe-Seyler have studied the action of **calcium carbonate** on soln. of magnesium sulphate.

According to H. Schiff, aq. soln. containing 10, 20, and 40 per cent. of *ethyl alcohol* dissolve respectively 64·7, 27·1, and 1·65 per cent. of heptahydrated magnesium sulphate at 10°. At higher temp., said A. Gérardin, the solubility increases proportionally with the temp. C. A. L. de Bruyn found that 100 grms. of absolute ethyl alcohol, at 3°, dissolved 13 grms. of the heptahydrate, and 100 grms. of absolute *methyl alcohol*, at 18°, dissolved 1·18 grms. of anhydrous magnesium sulphate, 41 grms. of the heptahydrate at 17°, and 29 grms. of the heptahydrate at 3° to 4°; while 100 grms. of 93 per cent. methyl alcohol dissolved 9·7 grms. of the heptahydrate at 17°, and 100 grms. of 50 per cent. methyl alcohol dissolved 4·1 grms. of the heptahydrate at 3° to 4°. According to W. Eidmann, magnesium sulphate is insoluble in *acetone*, and J. F. Snell found that with acetone and water, the soln. separates into layers with certain concentrations. J. Timmermans studied the ternary system *phenol*, magnesium sulphate, and water. A. Köhler found 100 grms. of a sat. soln. at 31·25° contained 46·52 grms. of *sugar* and 14 grms. of magnesium sulphate; 100 grms. of water dissolve 119·6 grms. of sugar and 36 grms. of magnesium sulphate.

The physical properties of magnesium sulphate.—The **crystals** of monohydrated magnesium sulphate were found by G. Tschermak [8] to be monoclinic pyramids with axial ratios $a:b:c=0·9147:1:1·7455$, and $\beta=91°\ 7'$. G. Wyrouboff found the crystals of the tetrahydrate to be monoclinic prisms, with $a:b:c$

$=0{\cdot}450 : 1 : ?$, and $\beta=90°\ 11'$; while the pentahydrate forms triclinic pinacoids, with $a : b : c=0{\cdot}6021 : 1 : 0{\cdot}5605$, and $\alpha=81°\ 30'$, $\beta=109°\ 0'$, and $\gamma=104°\ 55'$. L. de Boisbaudran found the crystals of β-$MgSO_4.6H_2O$ to be tetragonal pyramids; and those of α-$MgSO_4.6H_2O$ were found by J. C. G. de Marignac to be monoclinic prisms with axial ratios $a : b : c=1{\cdot}4039 : 1 : 1{\cdot}6683$, and $\beta=98°\ 34'$. J. C. G. de Marignac regarded the crystals of β-$MgSO_4.7H_2O$ as trigonal, but H. Kopp supposed them to be monoclinic prisms, and B. Gossner recalculated the measurements and obtained the axial ratios $a : b : c=1{\cdot}220 : 1 : 1{\cdot}582$, and $\beta=104°\ 24'$. From H. J. Brooke's measurements it follows that α-$MgSO_4.7H_2O$, or epsomite, forms rhombic crystals with axial ratios $a : b : c=0{\cdot}9901 : 1 : 0{\cdot}5709$. H. Grandinger made observations on this subject. E. Blasius, and J. Grailich have studied the **corrosion figures** of epsomite. The latter salt is the ordinary form of magnesium sulphate; it readily forms supersaturated soln., and, according to J. M. Thomson, the seeding of such soln. with crystals of zinc, nickel, iron (ous), or cobalt sulphate causes crystallization, but this is not the case when the soln. is seeded with crystals of sodium chloride, thiosulphate, or with potassium magnesium sulphate.

The reported numbers for the **specific gravity** of anhydrous magnesium sulphate, $MgSO_4$, range from C. J. B. Karsten's[9] 2·6066; E. Filhol's 2·628; C. Pape's 2·675 (16°); L. Playfair and J. P. Joule's 2·706; T. E. Thorpe and J. I. Watts' 2·709 at 15°; to O. Pettersson's 2·770 at 13·8° and 2·795 at 14°. H. G. F. Schröder gave 2·829, and if prepared by dehydrating the ordinary salt without fusion, 2·480. The sp. gr. of monohydrated magnesium sulphate, $MgSO_4.H_2O$, in the form of kieserite was given by F. Bischof as 2·517; and G. Tschermak gave 2·569. For the artificial salt H. G. F. Schröder gave 2·385; L. Playfair and J. P. Joule, 2·478; C. Pape, 2·281 at 16°; O. Pettersson, 2·339 at 14°; and T. E. Thorpe and J. I. Watts, 2·445 at 15°. For the sp. gr. of dihydrated magnesium sulphate, $MgSO_4.2H_2O$, L. Playfair and J. P. Joule gave 2·279; and T. E. Thorpe and J. I. Watts, 2·373 at 15°. For the sp. gr. of pentahydrated magnesium sulphate, $MgSO_4.5H_2O$, L. Playfair and J. P. Joule gave 1·869; G. Wyrouboff, 1·718; and T. E. Thorpe and J. I. Watts, 1·869 at 15°. Similarly, for monoclinic hexahydrated magnesium sulphate, $MgSO_4.6H_2O$, L. Playfair and J. P. Joule gave 1·751, and T. E. Thorpe and J. I. Watts, 1·734 at 15°. According to C. R. Schulze, the sp. gr. of the two modifications of the hexahydrate are respectively 1·8981 and 1·6151. J. W. Retgers gave 1·691 at 16° for the sp. gr. of labile monoclinic heptahydrated magnesium sulphate. A large number of determinations of the sp. gr. of rhombic heptahydrated magnesium sulphate have been made, and the results range from J. D. Forbes' 1·636 at 15·5° to E. Filhol's 1·571. Other determinations were made by J. H. Hassenfratz, 1·6603; H. Kopp, 1·674; L. Playfair and J. P. Joule, 1·6829 at 4°; H. Schiff, 1·685; H. J. Buignet, 1·675; S. Holker, 1·665 at 15·5°; C. Pape, 1·701 at 16°; O. Pettersson, 1·688; H. G. F. Schröder, 1·678; W. C. Smith, 1·632; J. W. Retgers, 1·678 at 16°; and T. E. Thorpe and J. I. Watts, 1·678 at 15°. G. Krause gave 1·61 to 1·71 for the sp. gr. of reichardite, and 2 to 3 for its **hardness**; the hardness of kieserite is 3. The **specific volumes** of magnesium sulphate and its hydrates, determined by T. E. Thorpe and J. I. Watts, are:

Hydrate .	0	1	1¼	2	4	5	6	7
Mol. wt. .	120	138	—	156	—	210	228	246
Sp. vol. .	44·8	55·6	—	67·0	—	112·4	130·8	146·6

The mol. vol. of the dissolved magnesium sulphate, calculated from the sp. gr. of the aq. soln., is zero in 0·3*N*-soln., and increases with a rising positive value as the conc. is augmented. L. de Boisbaudran,[10] and J. H. Pollok found a contraction occurs when the heptahydrate crystallizes from a supersaturated soln. According to R. Broom, if a soln. of 30·5 grms. of anhydrous magnesium sulphate in 100 c.c. of water be mixed with an equal volume of water, a percentage contraction 0·677 occurs. E. F. Anthon, A. Michel and L. Krafft, W. W. J. Nicol, H. Schiff, and A. C. Oudemans have measured the sp. gr. of soln. sat. at different temp.

G. T. Gerlach measured the sp. gr. of aq. soln. of magnesium sulphate at 15°, and making a selection from these values,

Per cent. $MgSO_4$.	1	2	5	10	15	20	25
Sp. gr. . . .	1·01031	1·02062	1·05154	1·10529	1·16222	1·22212	1·28478

H. T. Barnes and A. P. Scott also measured the sp. gr. of soln. with 2·01 to 26·25 per cent. of $MgSO_4$ at 18·2°; and J. G. McGregor over the range 0·191 to 1·132 per cent. of $MgSO_4$ at 19·5°. The latter represented his results at 20° by the formula $S=S_t+0·0106324w$, where w denotes the percentage composition, and S_t the sp. gr. of water; at 23°, the constant is 0·0098176. F. Kohlrausch and W. Hallwachs, O. Pulvermacher, and several others have made more or less subsidiary determinations—*e.g.*, H. C. Jones and F. H. Getman, D. Dijken, J. Forchheimer, O. Schönrock, W. Ostwald, J. Kannonikoff, C. A. Valson, J. Thomsen, S. Charpy, P. Barbier and L. Roux, E. Forster, H. Hager, P. de Heen, A. Sprung, R. J. Holland, H. Sentis, O. Knöfler, etc.

The **viscosity** of aq. soln. of magnesium sulphate has been measured by S. Arrhenius, O. Pulvermacher, W. W. J. Nicol, and J. Wagner. The latter found at 25° for N-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{8}N$-soln., the respective viscosities 1·3673, 1·1639, 1·0784, and 1·0320, when water is unity. H. Sentis, A. Battelli and A. Stefanini, and W. Grabowsky have measured the **surface tension** of soln. of magnesium sulphate. The latter found for the surface tension σ and the capillary constant a^2

	10°			30°		
Per cent. $MgSO_4$ . .	10·63	18·83	21·35	10·63	18·83	33·6
a^2 sq. mm. . . .	13·94	13·21	13·05	13·45	12·79	12·45
σ dynes per cm. . .	76·2	78·4	79·3	73·0	75·5	79·2

P. G. Tait found the **compressibility** of 16·06, 10·51, and 6·23 per cent. aq. soln. of magnesium sulphate to be $\beta\times10^6=29·6$, 33·5, and 36·5 respectively. W. Watson also measured this constant. T. Graham experimented on the diffusion of magnesium sulphate in aq. soln. J. D. R. Scheffer measured the **diffusion coefficient,** k, of magnesium sulphate and at 5·5°, found that for soln. with 0·54 and 2·18 mols per litre, k is 0·32 and 0·28 respectively, and at 10° for soln. with 0·40 and 3·23 mols per litre, k is 0·34 and 0·27 respectively; similarly, J. Schuhmeister found that k is 0·28 for a soln. with 1·7 mols per litre at 10°. W. Stiles found that the rate of diffusion in 0·5 per cent. agar-agar is nearly the same as in water; and in 10 per cent. gelatine, the rate is decreased nearly 25 per cent.

S. de Lannoy measured the thermal expansion of soln. of magnesium sulphate, and he found that with 3·796 per cent. of heptahydrated magnesium sulphate, for a temp. θ, between 0° and 40°, $v=v_0(1-0·0_5\theta+0·0_65585\theta^2)$; and between 40° and 75°, $v=v_0(1+0·0_4591\theta+0·0_5397\theta^2)$; for soln. with 9·915 per cent. of the heptahydrate, between 0° and 40°, $v=v_0(1+0·0_4708\theta+0·0_5431\theta^2)$, and between 40° and 85°, $v=v_0(1+0·0_31037\theta+0·0_53453\theta^2)$; for soln. with 19·688 per cent. of the heptahydrate, between 0° and 40°, $v=v_0(1+0·0_3139\theta+0·0_5335\theta^2)$, and between 40° and 82°, $v=v_0(1+0·0_3162\theta+0·0_52775\theta^2)$; while for soln. with 24·437 per cent. of the heptahydrate, between 0° and 82°, $v=v_0(1+0·0_32079\theta+0·0_5224\theta^2)$. E. Wiedemann found the thermal expansion up to 50° to be quite regular, when the vol. abruptly increases, owing to the elimination of water by the salt: $MgSO_4.7H_2O \rightarrow MgSO_4.6H_2O+H_2O$, and then expands quite regularly up to 93°; between 93° and 100° there is a marked contraction, and this is subsequently followed by a regular expansion.

According to G. H. Bailey,[11] when magnesium sulphate moistened with sulphuric acid is heated to 360°, all the free sulphuric acid is expelled and the weight remains constant up to 450°. R. Reidenbach found the weight of anhydrous magnesium sulphate remains constant from 650° to 700°, but dissociation begins at 750°, and is completed at 850°. G. H. Bailey added that when the sulphate is ignited for the oxide, a trace of sulphuric acid is retained very tenaciously even after a prolonged

ignition. C. Daubeny found that the sulphate lost about a quarter of its contained sulphur trioxide when heated for 3 hrs. at a bright red heat; and he stated that if heated for a still longer time, the cold product gives a residue insoluble in water, and which gives off some hydrogen sulphide when treated with acids. J. B. J. D. Boussingault stated that when small quantities are heated in the blast-flame, all the sulphur trioxide can be expelled. H. le Chatelier stated that the decomposition of the sulphate begins at 1160°. A. S. Ginsberg gave 1120° for the **melting point** (f.p.) of molten magnesium sulphate, and R. Nacken, 1124°. The latter stated that the salt is considerably decomposed at its m.p. According to G. J. Mulder, heptahydrated magnesium sulphate, in dry air for 45 days, loses 8·3 to 9·1 per cent. of water, and its composition remains constant; and, according to T. Graham, if kept at 22° in vacuo, or at 100° in air, rather more water than is required for the dihydrate remains; at about 130° the monohydrate is formed, and the latter loses all its combined water at a higher temp.—*vide* preparation of the anhydrous sulphate. According to G. J. Mulder, the per cent. water which is lost after heating to:

	40°	60°	82°	101°	119°	172°	201°
Water lost	8·7	33·2	34·7	34·7	40·5	40·8	41·5
Mol. eq.	H_2O	$3{\cdot}5H_2O$	—	$5H_2O$	—	—	$6H_2O$

The theoretical loss for the whole of the water in the heptahydrate is 51·2 per cent. H. G. F. Schröder found dehydration was complete in vacuo at 180°; and V. A. Jacquelain found that the salt which has lost 12·4 per cent. of water in vacuo, regains all the lost water on exposure to air. J. B. Hannay found the dehydration curve of the heptahydrate at 100° has breaks indicating the formation of the dihydrate and of *trihydrated magnesium sulphate*, but there is no other evidence in favour of the individuality of the trihydrate. See the individual hydrates for their temp. of formation.

According to C. Pape,[12] the **specific heat** of solid anhydrous magnesium sulphate is 0·225 between 25° and 100°; and, according to H. Kopp, the sp. ht. of heptahydrated magnesium sulphate is 0·3615 between 20° and 42°; C. Pape gave 0·407 for the heptahydrate between 15° and 28°; and 0·265 for the monohydrate between 25° and 100°. J. C. G. de Marignac found that the sp. ht. of aq. soln. of magnesium sulphate containing n mols of water per mol of $MgSO_4$, are 0·8690, 0·9230, and 0·9550, when n=50, 100, and 200 at 22·52°. G. Tammann measured the sp. ht. of dil. soln.; and other determinations have been made by K. Bindel, S. Pagliani, J. Thomsen, and H. Teudt. G. Jäger found the **thermal conductivity** of a 22 per cent. soln. of magnesium sulphate to be 97·5 when that of water is 100.

E. Cohen,[13] and P. C. F. Frowein have measured the **vapour pressure** of heptahydrated magnesium sulphate; the former's results above 30·75°, and the latter's results below that temp., are:

	14·95°	25·75°	30·75°	40·04°	41·42°	43·40°	47·45°
Vap. press.	4·93	12·29	18·34	37·90	41·89	43·37	64·31 mm.

P. C. F. Frowein obtained 18·35 mm. for the vap. press. of hexahydrated magnesium chloride at 30·75° This number is probably low, since E. Cohen obtained 18·96 mm. and H. Bolte 18·92 mm. The vap. press., p, obtained by H. W. Foote and S. R. Scholes; and p' by H. Bolte, are, at 25°,

	$0{-}1H_2O$	$1{-}4H_2O$	$4{-}5H_2O$	$5{-}6H_2O$	$6{-}7H_2O$
p mm.	1·0	4·9	8·8	9·8	11·5
p' mm.	—	4·6	7·9	10·1	12·0

For the 6–7 hydrate, P. C. F. Frowein gave 11·5 mm.; H. Lescœur, 11·7 mm.; E. Cohen, 12·0 mm.; W. C. Schumb, 12·50 mm.; and G. Wiedemann, 18·0 mm. at 25°. A. W. C. Menzies showed that there are initial disturbances in the observed results due to the redistribution of absorbed air by the salt and apparatus. H. Lescœur found the vap. press. of a sat. soln. of magnesium

sulphate at 20° to be 5·75 mm. G. Tammann found that with soln. containing 10·43, 25·33, and 50·74 grms. of $MgSO_4$ in 100 grms. of water, the vap. press. at 100° was lowered respectively 10·8, 26·4, and 82·7 mm.; and with soln. containing 6·33, 26·10, and 48·71 grms. of $Mg(HSO_4)_2$ in 100 grms. of water, the vap. press. at 100° was lowered 10·3, 57·0, and 136·1 mm. respectively. Measurements were also made by C. D. Carpenter and E. R. Jette. According to H. C. Jones and F. H. Getman,[14] the molecular **freezing point** lowering has a minimum with 0·48*N*-soln. This has been also studied by T. G. Bedford, H. Hausrath, F. M. Raoult, L. Kahlenberg, E. H. Loomis, S. Arrhenius, and A. A. Noyes and F. G. Falk. From these observations:

Grms. $MgSO_4$ per 100 grms. H_2O	0·00141	0·02867	0·699	2·534	9·768	18·343
Lowering of f.p.	0·000433°	0·007382°	0·154°	0·469°	1·629°	3·471°
Mol. lowering of f.p.	3·70°	3·10°	2·65°	2·23°	2·01°	2·08°

The **boiling point** of a sat. soln. is 105°, according to T. Griffiths, and G. J. Mulder, 108·4°; G. T. Gerlach found soln. with 8·8, 39·5 and 75 grms. of $MgSO_4$ in 100 grms. of water boiled respectively at 100·5°, 103°, and 108°. L. Kahlenberg found the raising of the b.p. of soln. with 2·733, 7·236, 43·47, and 72·28 grms. $MgSO_4$ per 100 grms. of water was respectively 0·097°, 0·281°, 1·455°, and 3·630°, and the mol. raising of the b.p. respectively 0·43°, 0·47°, 0·403°, and 0·605°.

According to J. Thomsen,[15] the **heat of formation** is (Mg, O, SO_3, aq.)=180·18 Cals.; and (Mg, O_2, SO_2)=232·31 Cals. M. Berthelot gave (Mg, S, $2O_2$)=309·0 Cals., and he also found for ($Mg(OH)_{2\text{precipitated}}$, $H_2SO_{4\text{aq.}}$)=31·2 Cals. J. Thomsen's values for the **heat of hydration** with the 1st, 2nd, 3rd, . . . and the 7th mols of water are:

1st	2nd	3rd	4th	5th	6th	7th
6·98	2·25	3·60	3·21	2·23	2·11	3·70 Cals.

F. Rüdorff found the temp. fell from 19·1° to 3·1° on mixing 85 parts of the heptahydrate with 100 parts of water. T. Graham concluded from his observations on the heat disengaged in the combination of dehydrated magnesium sulphate with water that "of the whole heat evolved in the complete hydration of magnesium sulphate, as nearly as possible one-fourth is due to the combination of the first mol. of water." S. U. Pickering's values for the **heat of solution** in 420 mols of water per mol $MgSO_4$, at 22·2°, are 20·765 Cals. for the anhydrous salt, 12·131 Cals. for the monohydrate, and −3·86 to −3·915 Cals. for the heptahydrate. J. Thomsen found for the heat of soln. in 400 mols of water per mol of the sulphate:

nH_2O	0	1	2	3	4	5	6	7
Cals.	20·28	13·30	11·05	7·45	4·24	2·01	−0·10	−3·80

M. Berthelot and L. Ilosvay de N. Ilosva represent the heat of soln. of the anhydrous sulphate in water at $\theta°$ by $20000+0·00007(\theta-15)$. C. M. van Deventer and H. J. van de Stadt give −4·1 Cals. for the integral heat of soln.

According to G. Tschermak,[16] the monohydrated sulphate has a positive **double refraction**; so also, according to G. Wyrouboff, has the tetrahydrate, while the pentahydrate and the hexahydrate have a negative double refraction; and, according to A. des Cloizeaux, the rhombic heptahydrate has also a negative double refraction. The **indices of refraction** of crystals of heptahydrated magnesium sulphate for the *D*-line have been determined by F. Kohlrausch, H. Dufet, and A. Fock, while H. Töpsöe and C. Christiansen found:

	μ_α	μ_β	μ_γ
F-line	1·4374	1·4607	1·4657
D-line	1·4325	1·4554	1·4608
C-line	1·4305	1·4530	1·4583

C. Borel also made determinations over the range $\lambda=226$ to $\lambda=718$. The index of refraction of soln. of magnesium sulphate has been measured by W. Hallwachs,

O. Pulvermacher, B. Wagner, J. Dinkhauser, and D. Dijken. The sp. refractive power of the solid salt (calculated from measurements on soln.) was found by E. Forster to be 0·2102 at 24°. P. Barbier and L. Roux measured the dispersion of soln., and D. Dijken, the mol. refraction and dispersion. According to J. Forchheimer, the **magnetic rotatory power,** or the specific electromagnetic **rotation of the plane of polarization** of 0·934*N*-, 1·86*N*-, and 2·73*N*-soln. is 0·306, 0·313, and 0·305 respectively, and the mol. electromagnetic rotation of the plane of polarization, 2·04, 2·02, and 2·03 respectively. This constant is therefore independent of conc. O. Schönrock gave 0·2978 for the specific rotation and 1·986 for the mol. rotation. L. Longchambon found the rotatory power of heptahydrated magnesium sulphate is 19° 15′ for both axes. According to P. Bary, anhydrous magnesium sulphate does not fluoresce on exposure to **X-rays** or to **Becquerel's rays.**

The **electrical conductivity** of molten magnesium sulphate and of mixtures with potassium sulphate has been measured by A. Benrath and K. Drekopf [17]; the electrical conductivity of aq. soln. of magnesium sulphate has been measured by W. C. D. Whetham, E. Klein, etc. P. Walden found the conductivity, λ, for an eq. of the salt in v litres to be :

v	32	64	128	256	512	1024
λ	73·0	83·0	92·6	101·8	110·1	116·9

H. C. Jones also measured the mol. conductivity, μ, and calculated the percentage **degree of ionization** α, and the **temperature coefficient,** k, of the mol. conductivity between 0° and 10° ; he found at 0° :

v	2	8	16	32	128	512	1024	2048
μ	32·12	45·70	50·95	59·57	71·17	95·57	102·7	111·1
α	28·9	41·1	45·9	53·6	64·1	86·0	92·4	100·0
k	1·10	1·52	1·71	2·01	2·42	3·27	3·57	3·74

Analogous results were obtained at 10°, 25°, 35°, 50°, and 65°. J. Kendall and co-workers measured the conductivity of soln. in anhydrous sulphuric acid. G. N. Lewis and G. A. Linhart measured the **degree of ionization** of dil. soln. of magnesium sulphate ; and G. N. Lewis and M. Randall, the activity coeff. of the ions. The **transport numbers** of the ions have been studied by W. Hittorf, A. Chassy, B. D. Steele, W. Bein, K. Hopfgartner, R. B. Denison, and O. Masson. C. Heim found no sudden change in the electrical conductivity on passing from a state of supersaturation to a state of ordinary soln. According to C. Borel,[18] the **dielectric constants** k_1, k_2, and k_3 of epsomite are respectively 8·28, 6·05, and 5·26 ; A. de Gramont studied the **pyroelectricity** of epsomite. J. Grailich and V. von Lang found that the crystals are feebly diamagnetic. The **magnetic susceptibility** of anhydrous magnesium sulphate at 18° and 19° was found by G. Quincke, and S. Meyer to be $-0{\cdot}36\times10^{-6}$ units ; C. K. Studley gave $-0{\cdot}46\times10^{-6}$, and G. Meslin, $-0{\cdot}62\times10^{-6}$; for the heptahydrated salt, S. Meyer gave $-0{\cdot}36\times10^{-6}$. P. Pascal gave 1357×10^{-7} units for the mol coeff. of magnetization.

The chemical properties of magnesium sulphate.—J. B. Richter [19] first noted the evolution of heat which occurs when magnesium sulphate, after ignition, is mixed with **water ;** and H. von Blücher noticed that the ignited salt gradually absorbed the eq. of $7H_2O$ from the air. When the sulphate is heated in a current of steam, G. Clemm noted that the sulphur trioxide can be all driven off. C. W. Scheele found " vitriolated magnesia " is but little affected by **hydrofluoric acid.** C. Hensgen found that **hydrogen chloride** begins to act on magnesium sulphate at a temp. approaching redness, and the reaction is not completed at this temp. in 3 hrs. A. B. Prescott found that when a gram of magnesium sulphate is evaporated to dryness with 4·035 grms. of hydrochloric acid containing 1·251 grms. of HCl, 0·003 grm. of magnesium chloride is formed. C. J. B. Karsten stated that magnesium sulphate melts when heated with **sodium chloride,** and this the more readily the greater the proportion of the latter salt ; and G. Clemm noted that when a mixture of the two salts is heated in a current of steam, hydrogen chloride

is evolved. V. Merz and W. Weith found that when melted in air with **potassium iodide,** iodine is set free. J. Zawadsky and co-workers obtained magnesia by the reduction of magnesium sulphate with **hydrogen sulphide.** According to J. L. Gay Lussac, when a mixture of anhydrous magnesium sulphate and **carbon** is heated to redness, a mixture of one vol. of carbon dioxide and two vols. of sulphur dioxide is obtained, some sulphur is liberated but no magnesium sulphide is formed; but P. Berthier obtained a trace of the sulphide when the reaction occurs at a white heat. E. Kunheim obtained similar results. E. H. Riesenfeld has studied the reduction, and found that there are concurrent reactions: $2MgSO_4+C=2MgO+2SO_2+CO_2$, and $MgSO_4+C=MgO+SO_2+CO$. According to K. Stammer, **carbon monoxide** has no action on red-hot magnesium sulphate; but, according to F. G. Reichel, magnesium oxide, carbonyl sulphide, and carbon dioxide are formed; while O. Boudouard obtained magnesia, and carbon and sulphur dioxides; J. Zawadsky and co-workers obtained in addition free sulphur; and, according to E. Jacquemin, in the presence of steam, carbon dioxide and hydrogen sulphide are formed. A recently prepared mixture of hydrated magnesium sulphate and **sodium hydrocarbonate** was found by L. A. Planche to dissolve in water without turbidity, but a similar mixture, after keeping some months, deposits magnesium carbonate. According to A. d'Heureuse, when a mixture of magnesium sulphate and **iron** is heated to redness, a little sulphur dioxide is evolved, and a mixture of magnesium and iron oxides with a little iron sulphide is formed; when **zinc** replaces the iron, a fulmination occurs. When a mixture of 33 grms. of heptahydrated magnesium sulphate, 5·5 to 9 grms. of **sodium hydroxide,** and 100 c.c. of water is heated between 195° and 205° for 31–55 hrs., two-thirds of the magnesium separates as hydroxide, and the remainder forms doubly refracting acicular crystals of **magnesium hydroxysulphate,** $6Mg(OH)_2.MgSO_4.3H_2O$, which are sparingly soluble in cold and hot water, but readily soluble in hydrochloric acid.

Magnesium sulphate is used in tanning leather, in sizing and loading cotton textiles; in weighting silk, paper, and leather; in dyeing; in enamelling industries; in fireproofing; in making paints and soaps; in the manufacture of mineral waters; and medicinally.

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§ 13. The Complex and Double Salts of Magnesium Sulphate

At least three double sulphates of sodium and magnesium occur in the Stassfurt salt deposits, namely, *vanthoffite*, $MgSO_4.3Na_2.SO_4$; *blödite* or *astrakanite*, or *simonyite*, $MgSO_4.Na_2SO_4.4H_2O$; and *löweite*, $MgSO_4.Na_2SO_4.2\frac{1}{2}H_2O$. R. Nacken,[1] S. Takegami, and A. S. Ginsberg have studied the equilibrium conditions in the binary system, $MgSO_4$—Na_2SO_4, and the probable results are shown graphically in Fig. 23. The equilibrium is somewhat complicated. The f.p. curve has a eutectic at 44·2 molar per cent. of $MgSO_4$, and 670°; and there is a break at 71·3 molar per cent. and 814°. α-Sodium sulphate forms solid soln. containing up to 35·8 mols per cent. $MgSO_4$. The compound **disodium trimagnesium tetrasulphate,** Na_2SO_4, $3MgSO_4$, melts with decomposition at 814°. Magnesium sulphate does not form solid soln. The existence of the two other compounds, **disodium magnesium disulphate,** Na_2SO_4, $MgSO_4$ and **hexasodium magnesium tetrasulphate,** $3Na_2SO_4$, $MgSO_4$, formed only in the solid state, is also indicated.

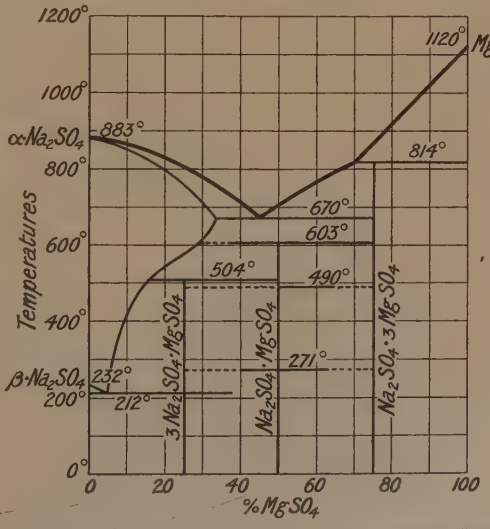

FIG. 23.—Freezing-point Curves of the Binary System, Na_2SO_4—$MgSO_4$.

These compounds are identical with anhydrous blödite and vanthoffite respectively, the former existing in α-, β-, and γ-modifications. Sodium sulphate only forms two modifications, the transition point being at 232°. H. le Chatelier placed the maximum at $Na_2SO_4.2MgSO_4$, but this is wrong. Some early work on the mutual solubilities of the sodium and magnesium sulphates has been previously indicated.

Crystals of löweite, *i.e.* **pentahemihydrated sodium magnesium disulphate,** $Na_2SO_4.MgSO_4.2\frac{1}{2}H_2O$, or $Na_2Mg(SO_4)_2.2\frac{1}{2}H_2O$, were found in masses associated with the anhydrite at the Ischl salt mine, Austria; and they were described by W. Haidinger in 1846, and analyzed by K. von Hauer. Löweite occurs in yellowish-white or reddish-white compact masses. J. H. van't Hoff and G. Just prepared this salt by dissolving 10·5 grms. of sodium chloride in a litre of water, and mixing this with a second soln. containing eq. proportions of magnesium and sodium sulphates. The mixed soln. is then slowly evaporated at 55° to 60°, when astrakanite begins to crystallize out. The soln. is then seeded with löweite, the vessel closed, and kept for several days at the same temp. Crystals of löweite appear. According to J. H. van't Hoff and A. O'Farelly, astrakanite is transformed into löweite at 71°; and a soln. which contains eq. proportions of the component salts, at a temp. exceeding 71° first gives astrakanite, which then passes into löweite. The transition temp. is lowered when other salts are present —*e.g.* it is 43° in the presence of a soln. containing 25 grms. of heptahydrated magnesium sulphate, 7 grms. of sodium chloride, 3 grms. of leonite, and one grm. of astrakanite. The optical properties of the crystals show that they belong to the tetragonal system. W. Haidinger found the sp. gr. of löweite to be 2·376 to 2·42; and the hardness $2\frac{1}{2}$ to 3 on Mohs' scale.

Reddish translucent masses of a mineral from the salt mines of Ischl (Austria) were analyzed by J. F. John in 1811, and found to be eq. to **tetrahydrated sodium magnesium sulphate,** $Na_2SO_4.MgSO_4.4H_2O$, or $Na_2Mg(SO_4)_2.4H_2O$. The mineral was called *blödite*, after M. Blöde. G. Rose obtained imperfect crystals from the salt lakes of Astrakan, east of the mouth of the Volga, and he called the mineral *astrakanite;* analyses showed that the two minerals have virtually the same composition. Crystals also occur in the soil near Mendoza, and east of San Juan, and at Stassfurt; and Munos y Luna found prismatic crystals in the dry beds of some Toledo lakes in summer. The salt has also been analyzed by K. von Hauer, A. A. Hayes, G. vom Rath, A. Brezina, etc. G. Tschermak obtained crystals of a mineral, which he called *simonyite*, resembling those of astrakanite, and of the same composition, but unlike the latter, the crystals of simonyite do not effloresce in air; and P. Groth and C. Hintze's blödite, which was unalterable in air, was probably simonyite; they assumed that the efflorescence of ordinary blödite was due to the presence of some efflorescent salt as impurity. H. F. Link regarded the double salt as a hexahydrate.

A. R. Arrott probably prepared tetrahydrated sodium magnesium sulphate in 1844, by evaporating at 50° a soln. containing eq. proportions of the component salts. J. Koppel, H. W. B. Roozeboom, J. H. van't Hoff and W. Meyerhoffer, and C. M. van Deventer and J. H. van't Hoff have studied the conditions under which the double salt is formed in aq. soln. The transition temp. for the reaction: $Na_2SO_4.10H_2O+MgSO_4.7H_2O \rightleftharpoons Na_2Mg(SO_4)_2.4H_2O+13H_2O$, is about 21·5°; and, according to the latter, if finely powdered astrakanite be mixed with water in the proportion represented by this equation, at a temp. below 21·5°, the thin paste soon sets to a dry solid mixture of the two sulphates, but above 21·5° this does not occur. Similarly, a finely powdered mixture of the two hydrated sulphates remains unchanged if kept in a closed flask below 21·5°, but above that temp. astrakanite is formed, and this is evidenced by the appearance of partial fusion produced by the liberated water. A mixture of heptahydrated magnesium sulphate and of decahydrated sodium sulphate melts at 26°. The formation of astrakanite is accelerated if some of the last-named salt be added at the beginning. The transi-

tion point is lowered by sodium chloride such that a mixture of eq. proportions of decahydrated sodium sulphate, heptahydrated magnesium sulphate, and sodium chloride melts at 15°, the system contracts, and monohydrated sodium sulphate separates out; after a time, the vol. increases, and astrakanite is formed. When this point is reached, the reverse reaction occurs below 5°—*cf.* Fig. 6, **2.** 20, 3. The formation of astrakanite by the reaction symbolized: $2MgSO_4.7H_2O+2NaCl=Na_2Mg(SO_4)_2.4H_2O+MgCl_2.6H_2O+4H_2O$, was found to occur above 30·6°.

Astrakanite is somewhat deliquescent in a moderately moist atm. J. Murray said the crystals are permanent in air. W. H. Miller found the axial ratios to be $a:b:c=1·3492:1:0·6717$, and $\beta=100°\ 48·5'$. This salt is one member of an isomorphous group in which manganese (ous), iron (ous), and zinc replace the magnesium of astrakanite; but it is not isomorphous with potassium-astrakanite. The crystals of astrakanite have a negative double refraction; the sp. gr. is 2·223 to 2·244; and the hardness 2·5 to 3·5 on Mohs' scale. According to J. H. van't Hoff and A. O'Farelly, astrakanite passes into löweite at 71°; and, according to J. H. van't Hoff and G. Just, in the presence of sodium chloride, and seeding with vanthoffite and löweite, the transition temp. is lowered to 59°. G. Tschermak found that the crystals lose about three-eighths of their water—*i.e.* 7·33 per cent. in weight—when heated on a water-bath; but P. Groth and C. Hintze found 8·8 per cent. is lost at 100°, and 10·12 per cent. at 150°; and G. vom Rath found 10·05 per cent. is lost between 100° and 130°; 10·09 per cent. between 130° and 300°; and the remaining 1·16 per cent. at a red heat. E. Reichardt also made observations on the dehydration of astrakanite. G. Tschermak found the dehydrated mass melts to a clear liquid which glows when it begins to freeze. J. H. van't Hoff and A. O'Farelly represented the vap. press., p, of astrakanite at a temp. θ, by the expression $\log p=\log p_w-(166·79-2·017\theta)/(273+\theta)$, where p_w represents the vap. press. of water. J. Murray said that the double sulphate is soluble in three times its wt. of water. According to H. W. B. Roozeboom, 100 mols of water hold in sat. soln.:

		22°	24·5°	30°	35°	47°
Astrakanite	Na_2SO_4	2·95	3·45	3·60	3·69	3·60 mols
	$MgSO_4$	4·70	3·68	3·60	3·69	3·60 „

If an excess of either component be present, the solubility of astrakanite is lowered a little. According to J. H. van't Hoff and A. O'Farelly, the heat of soln. of astrakanite is 1456 Cals. per kgrm. mol, and of löweite, 7998 Cals.; the heat of transformation of löweite to astrakanite is 6542 Cals. per kgrm. mol.

K. Kubierschky deduced indirectly that anhydrous **hexasodium magnesium tetrasulphate,** $3Na_2SO_4.MgSO_4$, or $Na_6Mg(SO_4)_4$, occurs in the salts from Wilhelmshall in the Magdeburg-Halberstadt salt district, and he gave it the name *vanthoffite*. J. H. van't Hoff found that the salt is produced artificially by heating the crystals of blödite, $Na_2Mg(SO_4)_2.4H_2O$, deposited at 22° from a soln. containing eq[uivalent] proportions of the component sulphates, which when heated to 70° in the liquor, lose some of their water, and are transformed into löweite, N[a]$_2$[Mg(SO$_4$)$_2$].$2\frac{1}{2}H_2O$, and at a still higher temp. crystals of the anhydrous salt appear. Among other methods of preparation, J. H. van't Hoff sh[owed] can be made by digesting on a water-bath a mixture of 154 grms. of sodium chloride, 252 grms. of decahydrated sodium chl[oride], heptahydrated magnesium sulphate; the sodium sulph[ate] gives way to vanthoffite, and when all is transforme[d] a hot-water suction filter, washed first with 50 [c.c.] alcohol and dried. According to J. H. van't [Hoff] temp. at which vanthoffite is formed from [the] soln. simultaneously saturated with sodi[um] of vanthoffite resemble those of löweite [and] the natural mineral, containing 10 p[er] cent.

C. H. Pfaff [2] found that magn[esium]

producing differently formed crystals—thus H. F. Link said that the crystals are long prisms which crumble in air; and C. L. Berthollet, that the crystals are rhombohedral and permanent in air. There are at least three double salts of magnesium and potassium sulphates in the Stassfurt salt deposits, namely, *langbeinite*, $2MgSO_4.K_2SO_4$; *leonite*, $MgSO_4.K_2SO_4.4H_2O$; and *picromerite* or *schönite*, $MgSO_4.K_2SO_4.6H_2O$. G. J. Mulder, and J. H. van't Hoff and N. Kassatkin prepared **pentahydrated potassium tetramagnesium pentasulphate,** $K_2SO_4.4MgSO_4.5H_2O$, or $K_2Mg_4(SO_4)_5.5H_2O$; the latter, by warming a mixture of hexahydrated magnesium sulphate with astrakanite at 72°, or by evaporating a soln. containing a mol of potassium sulphate and four mols of magnesium sulphate when needle-like crystals of leonite are first formed. The leonite finally disappears and the whole mass solidifies. Leonite alone does not form this compound. The transition point is given as 72·5°. It is regarded as a double salt of the hydrate $MgSO_4.1\frac{1}{4}H_2O$.

The mineral *langbeinite* was so named by S. Zuckschwerdt from specimens which he found near Halberstadt (Prussian Saxony). It occurs in the polyhalite regions at Wilhelmshall, and accompanies the sylvite at Westeregeln. The analyses agreed with anhydrous **potassium dimagnesium trisulphate,** $2MgSO_4.K_2SO_4$, or $K_2Mg_2(SO_4)_3$. G. J. Mulder made this compound in 1864; and F. R. Mallet obtained well-defined crystals by fusing together at a full red heat mol. proportions of the two components. The clear liquid, on cooling, generally intumesces. The best crystals were obtained by pouring the fused salt into a hot nickel crucible, and allowing the mass to cool. A. S. Ginsberg, and R. Nacken have studied the equilibrium conditions in the binary system, K_2SO_4—$MgSO_4$, and the results are shown graphically in Fig. 24.

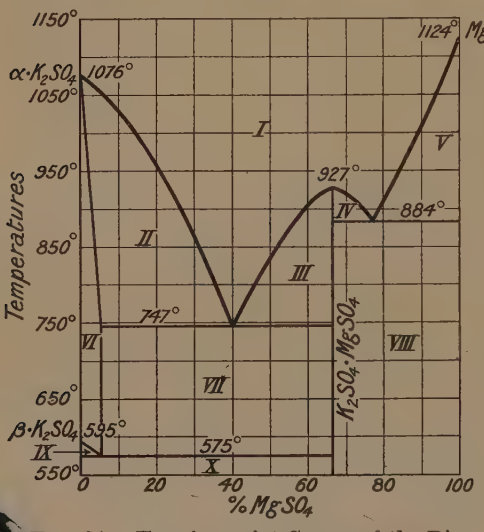

FIG. 24.—Freezing-point Curves of the Binary System, K_2SO_4—$MgSO_4$.

The two components are completely miscible in the molten state—region I; in region II, mixed crystals are in equilibrium with the melt, and in region VI the mixed crystals are alone stable. The first eutectic at 747°–750° corresponds with 38 to 40 molar per cent. of $MgSO_4$; the second eutectic at 884° has 78 molar per cent. of $MgSO_4$. In regions II, ... melt and langbeinite are coexistent, and in region VII langbeinite is in equilibrium ... ed crystals of VI. In region V the melt and magnesium sulphate crystals are ... d in region VIII langbeinite and magnesium sulphate are in equilibrium ... f VI are in equilibrium with β-K_2SO_4 in region IX, and, in region X, ... ilibrium with β-K_2SO_4.

... van't Hoff, W. Meyerhoffer, and F. G. Cottrell, the salt ... the component salts at 85°, and at a lower temp. in the ... like magnesium chloride; they recommended evaporat... of potassium sulphate, 49 grms. of heptahydrated ... s. of hexahydrated magnesium chloride, until ... nger dissolves, and then further evaporating ... ide begins to separate. The product is ... n nearly free from chlorides and water. ... to langbeinite is 89°, the transforma... at 100°, and requires a temp. of

120°. The temp. of formation of langbeinite from a mixture of leonite and hexahydrated magnesium chloride is 61°. The presence of hexahydrated magnesium sulphate depresses the temp. of formation of langbeinite from leonite, down to 61°; but this temp. may be easily passed without the change taking place, and at 72°, the unstable $K_2Mg_4(SO_4)_5.5H_2O$ is formed and readily passes into langbeinite when a little of the latter is present. The presence of sodium chloride lowers the temp. of formation still further.

According to O. Luedecke, crystals from Bernburg belong to the tetartohedral class in the cubic system; the octahedra obtained by F. R. Mallet are therefore supposed to be compounded of two tetrahedrons of opposite sign. The corresponding salts of zinc, manganese, and cobalt have the tetrahedron predominant. According to R. Nacken, the sp. gr. of the artificial salt is 2·829 at 25°; and O. Luedecke gives for the natural crystals 2·827 to 2·830. From the maximum in Fig. 24, the m.p. is 927°. The crystals are singly refracting, and, according to O. Luedecke, the index of refraction is 1·5281 for the Li-line, 1·5329 for the Na-line, and 1·5343 for the Tl-line. The crystals do not rotate the plane of polarization of light. F. R. Mallet observed that the salt gradually absorbs moisture from the atm. and decomposes into picromerite and epsomite: $K_2SO_4.2MgSO_4+13H_2O=MgSO_4.K_2SO_4.6H_2O+MgSO_4.7H_2O$. According to O. Schumann, when the double sulphate of magnesium and potassium is heated in a stream of hydrogen, hydrogen sulphide, sulphur, and water are formed, and a mixture of magnesium oxide and potassium sulphide remains. F. R. Mallet prepared **rubidium dimagnesium trisulphate,** $Rb_2SO_4.2MgSO_4$, or $Rb_2Mg_2(SO_4)_3$—this is *rubidium langbeinite*—in a similar way to that which he employed for langbeinite, and he found that it had similar properties.

No compound of the type *potassium magnesium disulphate*, $K_2SO_4.MgSO_4$, or $K_2Mg(SO_4)_2$, appears on the thermal diagram, Fig. 24, although M. Berthelot and L. Ilosvay de N. Ilosva claimed to have made it by fusing the component salts in the right proportions, and F. R. Mallet likewise claimed to have made this compound as well as rubidium magnesium disulphate by a similar process. He also made some measurements on the hygroscopic crystals. L. Playfair and J. P. Joule gave 2·676 for the sp. gr. of the crystals, and H. G. F. Schröder, 2·743.

According to A. Naupert and W. Wense, crystals of **tetrahydrated potassium magnesium disulphate,** $K_2SO_4.MgSO_4.4H_2O$, or $K_2Mg(SO_4)_2.4H_2O$, occur in the kainite beds of Westeregeln, and they are readily distinguished from the surrounding kainite; they also occur associated with the blue rock salt. At Leopoldshall, the mineral occurs as thick tabular crystals along with kainite and rock salt. The colour varies from a very pale yellow to a reddish, greyish-yellow. Analyses have been made by A. Naupert and W. Wense, C. A. Tenne, and J. E. Strandmark; the results are in agreement with the formula—the massive variety usually contains chlorides as impurities. This salt was obtained by J. K. van der Heide, by evaporating an aq. soln. of schönite and sodium chloride at 60°, or a soln. of magnesium and potassium sulphates at 100°. He called the salt *potassium astrakanite*, and it has also been called kaliblödite, but C. A. Tenne showed that there is no crystallographic relation between this mineral and blödite or astrakanite, and he therefore prefers the name *leonite*. The monoclinic prisms were found by C. A. Tenne to have axial ratios $a:b:c=1·03815:1:1·23349$, and the axial angle $\beta=84°\ 50'$. The optical axial angle is perpendicular to the plane of symmetry, and makes an angle 29° 30′ with the base. There is no distinct cleavage, and the fracture is conchoidal. J. E. Strandmark said that leonite is isomorphous with the artificial salt, $K_2Mn(SO_4)_2.4H_2O$, but not with astrakanite, $Na_2Mg(SO_4)_2.4H_2O$. Twinned crystals are found in the artificial preparations. The salt is soluble in water.

In his examination of the crystals of a salt produced at the eruption of Vesuvius in 1855, A. Scacchi found crystals of a mineral which was called *picromerite* in allusion to the magnesia present. The same crystals occur in the Stassfurt salt deposits along with kieserite and carnallite. Most of the impurities present as

chlorides can usually be removed by washing with alcohol. E. Reichardt called the mineral *schönite*—C. F. Zincken proposed kainite, but that name is reserved for another mineral. Analyses by M. Graf, E. Reichardt, R. Phillips, C. F. Rammelsberg, and others show that the composition is in agreement with **hexahydrated potassium magnesium disulphate,** $K_2SO_4.MgSO_4.6H_2O$, or $K_2Mg(SO_4)_2.6H_2O$. The crystals were obtained by A. Marcet from the bittern of sea-water, and by G. Busch from the mother liquid of the Lüneburg and Schönebeck springs. Schönite is obtained from soln. of potassium chloride and kieserite; from the leaching of kainite with water; and by evaporating the mixed soln. of the component salts to the point of crystallization.

According to T. C. McKay, when schönite is dissolved in water, it is decomposed more or less into its components, and from conductivity measurements, it follows that in conc. soln. some undecomposed double salt is still present, while in dil. soln., the salt is completely decomposed. The same conclusion follows from observations on the sp. gr. of aq. soln. which is smaller than that calculated for the components. The limits of existence and solubility relations have been described by J. K. van der Heide, J. H. van't Hoff, and H. S. van Klooster. The latter found that in aq. soln. of the two salts at 25°, the solid phase is $K_2Mg(SO_4)_2.6H_2O$ for conc. between 26·39 grms. of $MgSO_4$ and 7·02 grms. of K_2SO_4 per 100 grms. of sat. soln., where the solid phases are $MgSO_4.7H_2O$ and $K_2Mg(SO_4)_2.6H_2O$, and 12·68 grms. $MgSO_4$ and 10·70 grms. K_2SO_4, where the solid phases are $K_2Mg(SO_4)_2.6H_2O$ and K_2SO_4—*vide* the solubility of magnesium sulphate in soln. of potassium sulphate. J. K. van der Heide showed that schönite decomposes into its components below −3°, and above 72°; at 72°, in the presence of hexahydrated magnesium sulphate, schönite passes into leonite, and in the presence of potassium sulphate, the transition point is 92°. J. H. van't Hoff and P. Williams found that schönite passes into leonite at 47·5°, provided that an excess of potassium sulphate is present; at 41° if heptahydrated magnesium sulphate is present; and at 20° if the latter salt and also potassium chloride are present. Some equilibrium relations have been discussed in connection with Figs. 2–6, **2**. 20, 3. According to W. D. Bancroft:

> If one solid phase can be converted into one of the others by addition of water the inversion point is a maximum or a minimum temp. for one of those phases, and is neither a maximum nor a minimum for the third solid phase. For example, in the system: potassium sulphate, magnesium sulphate and water, at 47·2°, two of the phases are $MgSO_4.7H_2O$ and $MgSO_4.6H_2O$, the third is $K_2Mg(SO_4)_2.6H_2O$. This is a minimum temp. for the hexahydrate. The hydrated double salt exists both above and below the temp. of the inversion point. At 72° two of the solid phases are the hydrated double salts, $K_2Mg(SO_4)_2.6H_2O$ and $K_2Mg(SO_4)_2.4H_2O$, while the third is heptahydrated magnesium sulphate. At 92° two of the solid phases are the same two hydrated double salts and the third is potassium sulphate. The first temp. is a minimum for the double salt with four units of water, and the second a maximum for the one with six of water. If the temp. are not given it can only be told by experiment which point is which. If the compositions of the soln. are known, the direction of the temp. change can be foretold from the theorem of A. C. van Rijn van Alkemade that the temp. rises along the boundary curve in the direction of the line connecting the m.p. of the two solid phases. The higher temp. will necessarily be a maximum for the double salt with a larger amount of water of crystallization.

A. E. H. Tutton prepared the corresponding **hexahydrated rubidium magnesium disulphate,** $Rb_2Mg(SO_4)_2.6H_2O$, and **hexahydrated cæsium magnesium disulphate,** $Cs_2Mg(SO_4)_2.6H_2O$, by the evaporation of soln. of the component salts. The **crystals** have been measured by H. J. Brooke, C. F. Rammelsberg, A. Murmann and L. Rotter, H. Töpsöe and C. Christiansen, J. C. Heusser, F. L. Perrot, etc. They belong to the monoclinic system. The ammonium, potassium, rubidium, and cæsium salts form an isomorphous series. A. E. H. Tutton has made an exhaustive examination of the crystal constants of this series of salts and the corresponding series with zinc in place of magnesium, and with selenates in place of sulphates. He found the habit of the potassium salt is a stout primary prism with a large basal plane; that of the cæsium salt is a clinodome-prism with a narrow

basal plate ; and that of the ammonium salt gives all varieties. The axial ratios, the axial angle β, and the topic axes or distance ratios are indicated in Table I. The values for the ammonium salt are included.

TABLE I.—AXIAL RATIOS, TOPIC PARAMETERS, AND ANGLES OF THE SALTS : $M_2'Mg(SO_4)_2.6H_2O$.

	$a:b:c$	β	$\chi:\psi:\omega$	Sp. gr.	Mol. vol.
$K_2Mg(SO_4)_2.6H_2O$.	0·7413 : 1 : 0·4993	104° 48′	6·0711 : 8·1899 : 4·0892	2·034	196·58
$Rb_2Mg(SO_4)_2.6H_2O$.	0·7400 : 1 : 0·4975	105° 59′	6·1803 : 8·3518 : 4·1550	2·386	206·18
$(NH_4)_2Mg(SO_4)_2.6H_2O$	0·7400 : 1 : 0·4918	107° 6′	6·2320 : 8·4217 : 4·1418	1·723	207·78
$Cs_2Mg(SO_4)_2.6H_2O$.	0·7279 : 1 : 0·4946	107° 6′	6·2608 : 8·6012 : 4·2541	2·676	218·96

A. E. H. Tutton deduces the following relations : (1) The value of the axial angle β in the rubidium salt is approximately midway between the values of the axial angles of the potassium and cæsium salts. (2) The relative amounts of change brought about in the axial angle by replacing the alkali metal potassium by rubidium, and the rubidium in turn by cæsium, are approximately directly proportional to the relative differences in the at. wt. of the metals interchanged. (3) The axial angle increases with the increase in the at. wt. of the alkali metal. (4) The values of all the angles of the rubidium salt lie between the corresponding values of the potassium and cæsium salts, except in very rare cases, where more or less neutrality is produced owing to the changes in adjacent angles being of opposite sign. (5) The relative amounts of change in the angles other than the axial angle are rarely in direct simple proportion to the changes in at. wt. The maximum deviation from direct proportionality occurs in the prism zone at right angles to the zone containing the basal plane and orthopinacoid, and the relative amounts of change here bear the ratio of one to three. (6) The magnitude of the differences between most of the angular values of the three salts is surprisingly large, exceeding a whole degree in the cases of several important angles, and indicates a preponderating influence on the part of the alkali metals in determining the geometrical form of these double salts. (7) No indication of the full nature of the change brought about on replacing one metal by another in this isomorphous series is afforded by a comparison of the axial ratios, as simultaneous changes, which more or less neutralize each other, occur in the inclinations of the planes which determine them. The angles themselves alone furnish complete information concerning the change of external form. E. Blasius studied the corrosion figures of the ammonium salt.

J. W. Retgers found that the **specific gravity** of the mixed crystals of ammonium and potassium zinc sulphates varies linearly with the relative proportions of the two salts. The sp. gr. of the hexahydrated potassium salt has been found by L. Playfair and J. P. Joule to be 2·076 to 2·05319 at 4° ; H. Schiff gave 1·995 ; H. Töpsöe and C. Christiansen, 2·204 ; H. Gerhart, 2·029 ; and H. G. F. Schröder, 2·039. The latter's values for the sp. gr. of the potassium salt which has been dehydrated without melting, range from 2·735 to 2·750. F. L. Perrot found 2·41 for the sp. gr. of the rubidium salt, and G. Wulff, 2·672 for the cæsium salt. L. Playfair and J. P. Joule found for the hexahydrated ammonium salt 1·71686 at 4° ; H. Schiff, 1·608 ; H. J. Buignet, 1·762 ; H. Töpsöe and C. Christiansen, and F. L. Perrot, 1·720 ; G. Wulff, 1·721 ; and H. G. F. Schröder, 1·725. A. E. H. Tutton's values, for the sp. gr., at 20°, referred to water at 4°, and **molecular volumes** of the potassium, rubidium, ammonium, and cæsium series, are indicated in Table I. The rate of **diffusion** has been measured by C. Porlezza ; and the heat of admixture of soln. of the component salts by R. Dubrisay.

The **refractive indices** have been determined by H. Töpsöe and C. Christiansen, F. L. Perrot, and A. E. H. Tutton. The last-named has given the results in Table II.

TABLE II.—REFRACTIVE INDICES OF THE SALTS $M_2'Mg(SO_4)_2.6H_2O$ at 20°.

		Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
α	K	1·4581	1·4585	1·4607	1·4631	1·4658	1·4699
	Rb	1·4646	1·4650	1·4672	1·4695	1·4724	1·4762
	NH_4	1·4685	1·4689	1·4716	1·4740	1·4771	1·4814
	Cs	1·4828	1·4832	1·4857	1·4880	1·4912	1·4956
β	K	1·4603	1·4607	1·4629	1·4652	1·4678	1·4720
	Rb	1·4664	1·4668	1·4689	1·4713	1·4743	1·4782
	NH_4	1·4701	1·4705	1·4730	1·4755	1·4786	1·4831
	Cs	1·4830	1·4834	1·4858	1·4881	1·4912	1·4957
γ	K	1·4727	1·4731	1·4755	1·4778	1·4810	1·4853
	Rb	1·4755	1·4759	1·4779	1·4805	1·4835	1·4876
	NH_4	1·4756	1·4760	1·4786	1·4811	1·4842	1·4888
	Cs	1·4888	1·4892	1·4916	1·4940	1·4970	1·5015

The mean values for the refractive index and of the positive **double refraction** γ—α for Na-light, at 20°, are :

	K-salt.	Rb-salt.	NH_4-salt.	Cs-salt.
Mean refractive index	1·4664	1·4713	1·4744	1·4877
Double refraction	0·0148	0·0107	0·0070	0·0059

A. E. H. Tutton found the refractive indices of the potassium salt decrease by 0·0015 to 0·0022 in raising the temp. from 20° to 70° ; with the rubidium salt the decrease is about 0·0015 ; with the cæsium salt about 0·0016 ; and with the ammonium salt 0·0015 to 0·0019. The mean **molecular refractions** for the *C*-ray—Gladstone and Dale's formula—are 91·23 for the potassium salt, 96·74 for the rubidium salt, 98·03 for the ammonium salt, and 106·25 for the cæsium salt.

When the potassium salt is heated to 100°, it loses about 18·48 per cent. of water ; and T. Graham found all the water of crystallization is expelled at 132°. S. U. Pickering found the **heat of solution** of the dihydrated potassium salt to be 11·47 Cals. at 18° ; and of the hexahydrate, —9·96 Cals. J. Thomsen also gave for the heat of soln. of a mol of the salt $K_2SO_4.MgSO_4.nH_2O$, in 400 mols of water at 18° :

n	0	1	2	3	4	5	6 mols
Heat of soln.	10·60	6·122	0·741	—2·038	—5·160	—7·954	—10·024 Cals.

J. F. Daniell and W. A. Miller gave data for the **transport numbers** of the ions.

E. Erlenmeyer represents the constitution of $MgSO_4.K_2SO_4$ by $KO.SO_2.O.Mg.O.SO_2.OK$, otherwise expressed by $Mg(KSO_4)_2$. W. Meyerhoffer and F. G. Cottrell prepared what they called an acid triple salt, $KHMg(SO_4)_2.2H_2O$, or **potassium magnesium monohydro-disulphate,** $Mg(KSO_4)(HSO_4).2H_2O$, by dissolving leonite, $K_2SO_4.MgSO_4.4H_2O$, in 85 per cent. nitric acid and allowing the mixture to crystallize. The prismatic crystals are washed with absolute alcohol and ether, and dried at 60°. The crystals are doubly refracting. They are immediately decomposed by water, forming schönite, $K_2SO_4.MgSO_4.6H_2O$.

K. Kubierschky assumed the existence of a triple salt *potassium sodium magnesium sulphate,* and possibly related to the *sodium-potassium-simonyites* in the salt deposits of Wilhelmshall ; but J. H. van't Hoff and H. Barschall showed that isomorphous mixtures of astrakanite and leonite are involved, but no compound is formed.

E. Bechi [3] found ammonium sulphate with part of the alkali replaced by magnesium about the boric acid fumaroles of Tuscany ; and he named the mineral *boussingaultite ;* it has been described by O. Popp, who re-christened it *cerbolite.* It seldom occurs in a high degree of purity, but when recrystallized from water, analyses agree with its being **hexahydrated ammonium magnesium disulphate,** $(NH_4)_2SO_4.MgSO_4.6H_2O$, or $(NH_4)_2Mg(SO_4)_2.6H_2O$. According to J. J. Berzelius, the salt is readily precipitated as a crystalline powder on mixing conc. soln. of the

component salts ; or by passing ammonia into a soln. of magnesium sulphate in dil. sulphuric acid ; and its preparation and composition were studied by C. J. B. Karsten, T. Graham, etc. The crystallographic data, sp. gr., and optical constants have been discussed in connection with the corresponding potassium salt with which it is isomorphous. C. Borel found the dielectric constant of magnesium ammonium sulphate for $\lambda=\infty$, to be 8·54 for the symmetry axis. According to H. Rheineck, at 120°, the crystals lose 25·8–26·1 per cent. of water, and at a higher temp. they melt and decompose. The crystals, dried at 100°, were found by T. Graham to lose all their water and become anhydrous at 132°. H. G. F. Schröder gave 2·105 for the sp. gr. of the dehydrated salt. The crystals are less soluble in water than either of their component salts ; G. J. Mulder stated that at 13°, 100 parts of water dissolved 15·9 parts of $(NH_4)_2Mg(SO_4)_2$; and, according to E. Tobler, 100 grms. of water dissolve at :

	0°	10°	20°	30°	45°	50°	60°	75°
$(NH_4)_2Mg(SO_4)_2$ . .	9·0	14·2	17·9	19·1	25·6	30·0	36·1	45·8 grms.

J. Lothian obtained rather higher results ; he found that 100 grms. of water dissolved 18·22 grms. of the double salt at 1·1° ; 20·72 grms. at 5° ; 22·48 grms. at 10° ; 24·08 grms. at 15° ; 24·81 grms. at 15·5° ; 28·26 grms. at 20·5° ; and 33·33 grms. at 27·2°. According to C. F. Lindsay, the electrical conductivity of a conc. soln. is smaller than that of either of the components at the same conc. ; and H. C. Jones and B. P. Caldwell estimate that the salt is completely dissociated at a conc. of a 0·005*N*-soln. F. Rüdorff, D. M. Torrance and N. Knight, H. L. Maxwell, and C. Porlezza studied the dissociation of the salt by diffusion experiments. A. Weston studied the quaternary system : K_2SO_4—Mg_2SO_4—$(NH_4)_2SO_4$—H_2O. G. Spacu and R. Ripan prepared **magnesium tetraquodiamminosulphate,** $[Mg(NH_3)_2(H_2O)_4]SO_4$, as a crystalline powder ; **magnesium triaquotriamminosulphate,** $[Mg(NH_3)_3(H_2O)_3]SO_4$, in colourless crystals ; **magnesium diaquodiamminosulphate,** $[Mg(NH_3)_2(H_2O)_2]SO_4$, as a white powder. They also made complexes with piperidine, and benzylamine. G. Spacu made a complex with triethylenediamine.

The mineral *kainite* occurs as yellowish-greyish or greenish masses in the salt deposits of Stassfurt, Westeregeln, Kalucz in Galicia, etc. ; its name is derived from *καινός*, recent. Analyses correspond with **trihydrated potassium magnesium chlorosulphate,** $KCl.MgSO_4.3H_2O$, or possibly with $K_2SO_4.MgSO_4.MgCl_2.6H_2O$. The former was recommended by W. Meyerhoffer,[4] G. Tschermak, A. de Schulten, and E. Erlenmeyer, and the latter by A. Frank. The formula may also be written $Mg(KSO_4)Cl.3H_2O$.

$Mg<^{Cl}_{Cl}$	$Mg<^{Cl}_{KSO_4}$	$Mg<^{KSO_4}_{KSO_4}$	$Mg<^{HSO_4}_{KSO_4}$
Magnesium chloride.	Kainite.	Leonite or Schönite.	Monohydrodisulphate.

In 1843, C. J. B. Karsten noticed that no precipitation occurs on mixing conc. soln. of potassium chloride and magnesium sulphate, but crystals appear when the soln. has stood for some hours. A. de Schulten prepared kainite by evaporating on a water-bath a mixed soln. of 40 grms. of potassium sulphate and 80–90 grms. of magnesium sulphate with a great excess (500 grms.) of hexahydrated magnesium chloride. The crystals are removed from the mother liquid by press. or suction, and washed with absolute alcohol. If a smaller proportion of magnesium sulphate is employed, the product is contaminated with carnallite. The conditions of formation of kainite have been studied by J. H. van't Hoff and W. Meyerhoffer. The former showed that what he called a *tetragenic salt*—*i.e.* one with four different elements or radicles, exclusive of the water of crystallization—must have at least two and it may have three temp. of formation ; the temp. of formation of kainite are 76° and 85°, and the *polytherms*, or the equilibrium relationships of kainite at different temp., show that besides the above primary temp. of formation, other lower secondary temp. of formation exist.

The crystals of kainite were shown by P. Groth to be monoclinic prisms with axial ratios $a : b : c = 1{\cdot}2186 : 1 : 0{\cdot}5863$, and $\beta = 94° 54' 30''$. For this sp. gr. of kainite, C. F. Zincken gave 2·131; E. Reichardt, 2·133 to 2·154; V. von Zepharovich, 2·151; and A. de Schulten, 2·120, at 15°, for the artificial product. The hardness is 2·5 to 3·0. The double refraction is negative. According to C. F. Rammelsberg, kainite effloresces on standing over conc. sulphuric acid. C. F. Zincken, and A. Frank observed that kainite loses water and hydrogen chloride when heated. In moist air, water is absorbed, magnesium chloride is washed out, and schönite remains; water and alcohol decompose it in a similar way. According to G. Krause, 100 parts of water at 18° dissolve 79·56 parts of kainite; and J. G. Lehmann noted that a mixture of equal parts of alcohol and ether, which dissolves magnesium chloride, does not dissolve kainite.

The triple salts, *polyhalite*, $2CaSO_4.MgSO_4.K_2SO_4.2H_2O$, and *krugite*, $4CaSO_4.MgSO_4.K_2SO_4.2H_2O$, occur in the Stassfurt salt deposits. Polyhalite was named by F. Stromeyer [5] from πολύς, many, ἅλς, salt, in reference to the number of the component salts which make up the mineral. It occurs associated with gypsum, anhydrite, and rock salt in the salt deposits at Ischl, Ebensee, Aussee, Hallstadt, and Hallein in Austria; at Berchtesgaden in Bavaria; at Vic in Lorraine; and the various Stassfurt deposits. Analyses have been reported by F. Stromeyer, C. F. Rammelsberg, W. Dexter, C. A. Joy, K. von Hauer, P. Berthier, J. B. Schober, G. Jenzsch, F. Bischof, E. Reichardt, etc. In the main, these agree with the composition: $2CaSO_4.MgSO_4.K_2SO_4.2H_2O$, **dihydrated magnesium potassium dicalcium sulphate.** M. Rosza has shown that the occurrence of polyhalite in different parts of the salt deposits is in good agreement with the work of J. H. van't Hoff. A. Goebel found nodules of a white mineral resembling polyhalite, and associated with the carnallite of the salt mines at Maman (Persia), and hence named *mamanite*. The ratio of the calcium, magnesium, and potassium sulphates is as 3 : 2 : 1. According to J. H. van't Hoff and G. L. Voerman, mamanite is an impure polyhalite. According to E. E. Basch, polyhalite is formed at 25° in a soln. containing syngenite, gypsum, and epsomite. The region of its existence is narrow. Soln. containing per litre :—

K_2SO_4	$MgSO_4$	Solid phases.
3·5	56·7	Polyhalite, gypsum, syngenite
3·6	55·7	Polyhalite, gypsum, epsomite
5·1	58·1	Polyhalite, syngenite, epsomite

The equilibrium conditions are illustrated diagrammatically in Fig. 25, although H. S. van Klooster has shown that there is probably something wrong in E. E. Basch's results. Polyhalite is probably rhombic, its sp. gr. is 2·769, and its hardness 2·5 to 3. According to H. Rose, it melts when heated, and on cooling solidifies to an amorphous mass. Polyhalite is decomposed with difficulty by cold water, and leaves a residue of calcium sulphate, while potassium and magnesium sulphates pass into soln. It is more rapidly decomposed by hot water. The dehydrated salt hardens when mixed with water, and forms a voluminous mass, which is readily separated into its constituents by water. J. H. van't Hoff, F. Farup, and J. d'Ans have further studied the formation of polyhalite in the presence of "sea-salts."

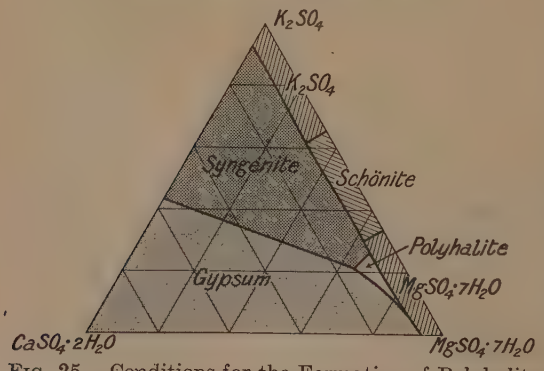

FIG. 25.—Conditions for the Formation of Polyhalite (25°).

H. Precht analyzed a crystalline mineral resembling polyhalite, which he found at the salt-works of New Stassfurt. Its analysis corresponds with $4CaSO_4.MgSO_4.K_2SO_4.2H_2O$, **dihydrated magnesium potassium tetracalcium sulphate,** and it is supposed to be a mixture of polyhalite and anhydrite, even though it appears homogeneous under the microscope. It was named *krugite* after the mining director, D. Krug von Nidda. The sp. gr. of krugite is 2·801, and its hardness 3·5. With cold water, magnesium sulphate is dissolved, and a double salt, $K_2SO_4.CaSO_4.H_2O$, remains insoluble, and with hot water, it acts like polyhalite, dissolving magnesium and potassium sulphates, and leaving the gypsum undissolved.

According to J. H. van't Hoff and A. P. Saunders,[6] if an aq. soln., containing the sulphates and chlorides of potassium, sodium, and magnesium, and sat. with sodium chloride, be evaporated at 25°, sodium and potassium chlorides; carnallite, $KMgCl_3.6H_2O$; bischoffite, $MgCl_2.6H_2O$; hexa- and hepta-hydrates of magnesium sulphate; schönite, $K_2Mg(SO_4)_2.6H_2O$; glaserite, $K_3Na(SO_4)_2$; penta- and tetra-hydrates of magnesium sulphate; thenardite, Na_2SO_4; and astrakanite, $Na_2Mg(SO_4)_2.4H_2O$, crystallize from the soln., but not langbeinite, $K_2Mg_2(SO_4)_3$; Glauber's salts, $Na_2SO_4.10H_2O$; nor löweite, $Na_2Mg(SO_4)_2.2H_2O$. The formation of potassium sulphate; kieserite, $MgSO_4.H_2O$; kainite, $KCl.MgSO_4.3H_2O$; and leonite, $K_2Mg(SO_4)_2.4H_2O$, occurs only under special conditions; for example, J. H. van't Hoff and P. Williams state that supersaturation phenomena prevent the appearance of leonite. J. H. van't Hoff and co-workers have shown that at 25°, soln. with 1000 mols of water sat. with one, two, three, or four other salts have the compositions, and vap. press. in mm. of mercury, shown in Table III.

Table III.—Limits of Existence of Salt Minerals.

1000 mols H_2O →	Na_2Cl_2	$MgCl_2$	K_2Cl_2	Na_2SO_4	$MgSO_4$	mm.
NaCl; $MgCl_2.6H_2O$	2·5	103 (24·9°)	—	—	—	7·63
NaCl; KCl	44·5	—	19·5	—	—	16·844
NaCl; Na_2SO_4	51	—	—	12·5	—	17·5
NaCl; $MgCl_2.6H_2O$; carnallite	1	103·5	0·5	—	—	7·52
NaCl; Carnallite; KCl	2	70·5	5·5	—	—	12·66
NaCl; KCl; glaserite	44	—	20	4·5	—	16·841
NaCl; Glaserite; Na_2SO_4	44·5	—	10·5	14·5	—	17
NaCl; Na_2SO_4; astrakanite	46	—	—	3	16·5	17·1
NaCl; Astrakanite; epsomite	26	7	—	—	34	15·1
NaCl; Epsomite; $MgSO_4.6H_2O$	10·5	53	—	—	15	12
NaCl; $MgSO_4.6H_2O$; $MgSO_4.5H_2O$	2	83·5	—	—	9	10·6
NaCl; $MgSO_4.5H_2O$; $MgSO_4.4H_2O$	1	86	—	—	8	9·3
NaCl; $MgSO_4.4H_2O$; $MgCl_2.4H_2O$	1	102	—	—	5	7·55
NaCl; Glaserite; schönite; KCl	23	21·5	14	14	15·9	—
NaCl; Leonite; schönite; KCl	14	37	11	14·5	14·9	—
NaCl; Leonite; $MgSO_4.6H_2O$; KCl	17	30·5	13	13·5	13·2	—
NaCl; $MgSO_4.6$ and $5H_2O$; KCl	8	63	6·5	5	—	—
$MgSO_4.5$ and $4H_2O$; carnallite; KCl	2·5	68	6	5	12·4	—
$MgSO_4.5$ and $4H_2O$; carnallite; $MgCl_2.6H_2O$	0	100	0·5	5	7·4	—
NaCl; Na_2SO_4; astrakanite; glaserite	40	2	8	8	14	—
NaCl; Astrakanite; glaserite; schönite	27·5	16·5	10·5	—	18·5	—
NaCl; Astrakanite; schönite; leonite	22	23	10·5	—	19	—
NaCl; Epsomite; astrakanite; leonite	10·5	42	7·5	—	19	—

J. H. van't Hoff represented these results graphically, and applied them to the phenomena which occur during the evaporation of sea-water, and which were studied by J. Usiglio. Kainite and kieserite did not appear owing to supersaturation; and when the effects of this phenomenon were eliminated, the compositions of the soln. sat. with different salts are shown in Table IV.

TABLE IV.—LIMITS OF EXISTENCE OF SALT MINERALS.

1000 mols H_2O sat. with	Na_2Cl_2	$MgCl_2$	K_2Cl_2	$MgSO_4$
Kainite ; NaCl ; epsomite ; leonite	9	45	7·9	19·5
Kainite ; NaCl ; KCl ; leonite	9·5	47	9·5	14·5
Kainite ; NaCl ; KCl ; carnallite	2·5	68	6	5
Kainite ; NaCl ; $MgSO_4.6H_2O$; carnallite	0·5	85·5	1	8
Kainite ; NaCl ; $MgSO_4.6H_2O$; epsomite	3·5	65·5	4	13
Kieserite ; NaCl ; $MgSO_4.6H_2O$	2·5	79	—	9·5
Kieserite ; NaCl ; carnallite ; kainite	0·5	85·5	1	8
Kieserite ; NaCl ; $MgSO_4.6H_2O$; kainite	1·5	77	2	10
Kieserite ; NaCl ; carnallite ; $MgCl_2.6H_2O$	—	100	0·5	5

The graphic representation of the results has been discussed by J. H. van't Hoff and W. Meyerhoffer, J. H. van't Hoff and F. Farup ; J. H. van't Hoff, H. Sachs, and O. Biach ; and E. Jänecke—the last-named also in his work : *Gesättigte Salzlösungen vom Standpunkt der Phasenlehre* (Halle, 1908).

The limits of existence of the different minerals with respect to temp. are indicated in Table V. In studying the *paragenesis*—παρά, beside ; γένος, birth—

TABLE V.—TRANSFORMATION TEMPERATURES OF SALT MINERALS.

Mineral.	Presence.	Absence.	Product.
Glauber's salt, $Na_2SO_4.10H_2O$	18°	32·5°	Thenardite, $NaSO_4$
Schönite, $K_2Mg(SO_4)_2.6H_2O$	26°	47·5°	Leonite, $K_2Mg(SO_4)_2.4H_2O$
Epsomite, $MgSO_4.7H_2O$	31°	48°	$MgSO_4.6H_2O$
$MgSO_4.6H_2O$	35·5°	67·5°	Kieserite, $MgSO_4.H_2O$
Astrakanite, $Na_2Mg(SO_4)_2.4H_2O$	59°	71°	Löweite, $Na_2Mg(SO_4)_2.2\frac{1}{2}H_2O$
Leonite, $K_2Mg(SO_4)_2.4H_2O$	61·5°	89°	Langbeinite, $K_2Mg_2(SO_4)_3$
Kainite, $KCl.MgSO_4.3H_2O$	83°	85°	Hard salt, $MgSO_4.H_2O$ and KCl

i.e. the origin of the salt minerals between 25° and 83°, it was found convenient to divide the temp. interval into three periods. The first ranges from 25° to 37°, and here the limits for the phases schönite, epsomite, and $MgSO_4.6H_2O$ gradually become less, or disappear, as illustrated diagrammatically in the schemes I to V, Fig. 26. The appearance or disappearance of a new phase is represented by a blackened circle. In the second period, between 37° and 55°, langbeinite, löweite, and vanthoffite appear as new phase, as illustrated in VI to VIII, Fig. 26. In the third period, ranging from 55° to 83°, astrakanite, löweite, and kainite disappear, as illustrated IX to XII, Fig. 26. Below 25°, many of the phases disappear, and at 18°, Glauber's salt appears, and kieserite disappears ; at 13·5°, thenardite disappears ; and at 13°, the hexahydrate, $MgSO_4.6H_2O$, disappears.

J. H. van't Hoff and co-workers [7] have also studied systems containing potassium, sodium, and magnesium chlorides and sulphates with calcium sulphate in addition. The range of existence of the different salt minerals is indicated. The limiting soln. for syngenite and polyhalite at 83° are indicated in Table VI.

TABLE VI.—LIMITS OF EXISTENCE OF THE SALT MINERALS AT 83°.

1000 mols of H_2O →	Na_2Cl_2	K_2Cl_2	$MgCl_2$	$MgSO_4$	Na_2SO_4	$CaSO_4$	$CaCl_2$
NaCl ; anhydrite ; glauberite	18	—	47.5	13·5	—	0·28	—
NaCl ; glauberite ; syngenite	40·5	33·5	—	—	6·5	small	—
Syngenite ; $K_2SO_4.5CaSO_4.H_2O$	40·5	38·5	—	—	2	0·18	—
Anhydrite ; $K_2SO_4.5CaSO_4.H_2O$	32	31	—	—	—	0·07	20·5
Glauberite ; polyhalite	43	23·5	—	7·5	5·5	0·08	—
Glauberite ; polyhalite ; syngenite	41·5	32	—	4·2	2·7	0·14	—
Syngenite ; polyhalite	40·5	37	—	3	2	0·14	—
Syngenite ; polyhalite ; $K_2SO_4.5CaSO_4.H_2O$	40·5	38	—	2·5	0·5	0·14	—

J. H. Hildebrand studied the systems $KCl-MgCl_2-K_2SO_4-MgSO_4$ at 25°; $NaCl-KCl-MgCl_2-MgSO_4-Na_2SO_4$ at 25°, and at 83°; and $NaCl-MgCl_2-MgSO_4-Na_2SO_4$ at 25°. W. C. Blasdale studied the system with water and the

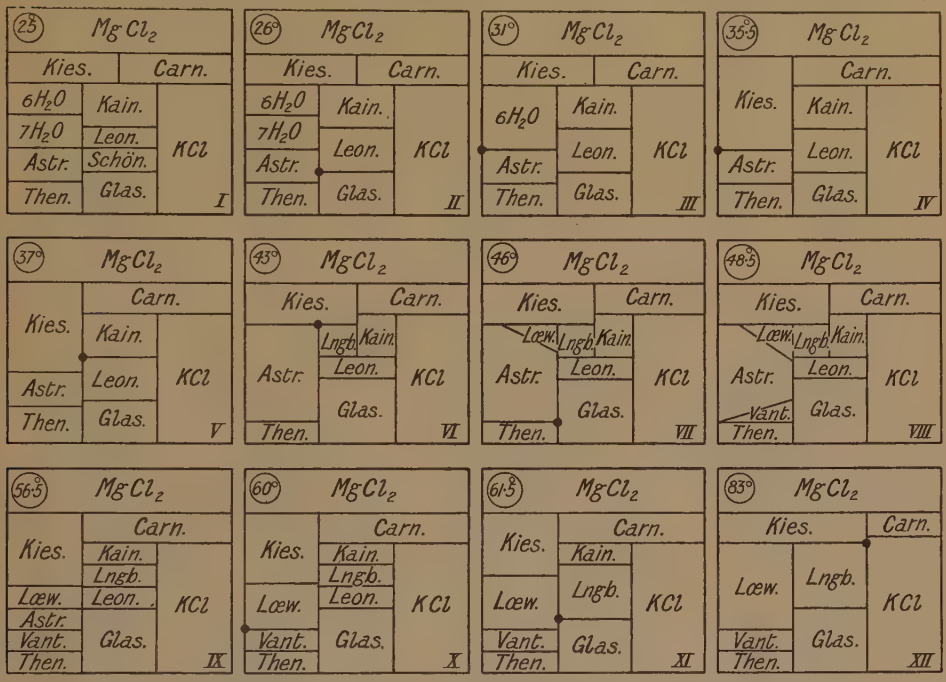

FIG. 26.—Paragenetic Relations of the Salt Minerals between 25° and 83°.

(Kies. =kieserite; Carn. =carnallite; $6H_2O$ and $7H_2O$ stand respectively for $MgSO_4.6H_2O$ and $MgSO_4.7H_2O$; Astr. =astrakanite; Then. =thenardite; Kain. =kainite; Leon. =leonite; Schön. =schönite; Glas. =glaserite; Vant. =vanthoffite; Loew. =löwite; and Lngb. =langbeinite.)

sulphates and chlorides of sodium and magnesium at different temp. S. Takegami studied the equilibrium of salt pairs—sodium and magnesium chlorides and sulphates at 25°.

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§ 14. Magnesium Carbonate

Anhydrous normal **magnesium carbonate,** $MgCO_3$, occurs in nature as the mineral *magnesite*. This was discovered at Hrubschütz (Moravia), and named *Kohlensaurer Talkerde* by W. A. Lampadius (1800); [1] and *reine Talkerde*, or *Talcum carbonatum*, by C. F. Ludwig (1803). J. C. Delamétherie (1795) applied the term magnesite to a series of magnesium salts—carbonate, sulphate, nitrate, and chloride; and A. Brongniart applied the same term to a group of minerals including magnesium carbonate, and a series of siliceous varieties. The carbonate came first in both series of magnesites, and the term magnesite was formally reserved for the carbonate by D. L. G. Karsten in 1808. This was gradually accepted by the German mineralogists, though, in France, F. S. Beudant's term *giobertite* for the carbonate, and his magnesite for the silicate prevailed for a long time. J. C. Delamétherie used *baudisserite* for a siliceous earthy variety from Baudissero near Turin which was analyzed by G. A. Giobert; this variety of magnesite resembles chalk, and sticks to the tongue.

There are two main types of magnesite—the one type is amorphous or a gel colloid, and is represented by the compact, granular, and cleavable forms; and the other type occurs in distinct rhombohedral or trigonal crystals. A. Breithaupt called the former *magnesite* and the latter *magnesite spar*; but magnesite is now applied to both forms. Magnesite usually contains some iron, possibly as ferrous carbonate, siderite, and the colour may be white, yellow, brown, or rarely black.

The light-coloured ferruginous magnesites often become brown on exposure; hence the name brown spar. A variety containing 5–10 per cent. ferrous oxide was called by W. Haidinger, after M. Breuner, *breunnerite*; and a variety analyzed by L. P. Walmstedt, containing a little more manganese oxide than usual was called *walmstedtite* by K. C. Leonhard. A. Breithaupt named one variety *mesitite* or *mesitine*—μεσίτης, a go-between—being intermediate in composition between siderite and magnesite; and another variety, with a little more iron and nearer the mean composition of magnesite and siderite, was called *pistomesite*—πιστός, truly.

Magnesite is formed in nature as a product of the action of carbonated waters on the more easily decomposed magnesium rocks—*e.g.* peridotites and serpentines.[2] The magnesia is dissolved as carbonate and may be deposited elsewhere along with more or less opaline silica formed at the same time. Ferrous carbonate may also be formed and produce a mixed carbonate. Instead of depositing their contained magnesium carbonate, these waters may act on limestone or dolomite, replacing the calcium by magnesium. Magnesite may also be formed as a sedimentary deposit, for H. S. Gale observed that near Bisnell, California, magnesian salt soln. mix with sodium carbonate, and deposit basic magnesium carbonate.

No deposits of magnesite of any industrial importance are known in the British Isles. Large deposits of crystalline magnesite occur in Austria and Hungary—principally

at Veitsch, and other places in Styria, and about Jolsva and Nyusta in N.-W. Hungary; they follow a N.-E. and N.-W. line crossing Vienna and Budapest. Deposits are also worked at Kraljevo, Serbia. There are very important deposits of chalk-like magnesite in the northern part of the Island of Eubœa, Greece; and there are deposits on the Chalcidice peninsula, Macedonia. In Italy, compact magnesite has been quarried at Castiglioncello, Monterufoti on the Island of Elba, and also in Turin. In Norway, spathic magnesite is worked at Snarum, Modum. In Russia, at Mt. Boltscheja, there are quarries of magnesite resembling that from Austria. There is a small output of compact magnesite from Spain—Esperanza and San Jose, Santander, and La Papa, Almeria. Large deposits of compact magnesite occur in the Barberton district, Eastern Transvaal, S. Africa. In India, compact magnesite is mined in the Chalk Hills of the Salem district, Madras; and there are deposits at Dod Kanya and Dod Katur, Mysore. Compact magnesite occurs in many parts of Australia—Fifield, N.S.W.; Heathcote, Victoria; Marlborough and Kunwarara, Queensland; Tumby Bay, South Australia; and at Bulong, Western Australia. In Canada there are large deposits of lenticular masses of magnesite in the Grenville district, Quebec; and in British Columbia there are deposits of compact magnesite and of hydromagnesite. Most of the magnesite mined in the United States is of the Grecian type and comes from California, where it occurs on the western side of the Sierra Nevada in the Tulare, Sonoma, Santa Clara, and Kern counties; and crystalline magnesite occurs in Stevens County, Washington. Compact magnesite occurs on the Island of Margarita, Venezuela. Compact magnesite also occurs in Manchuria. Bibliographies have been published by the Imperial Mineral Resources Bureau, etc.[3] There are many of the deposits in which the magnesite may occur in veins too thin to work profitably, and many would be workable if more favourably situated for transport.

Numerous analyses of selected specimens have been reported.[4] The material is blasted from the sides of the quarry, and broken to one-man pieces, and the particles of gangue—dolomite, quartz, serpentine, calcite, and other impurities—are removed by cobbing, etc. The extremes in some commercial samples of raw magnesite are indicated in Table VII. Small proportions of manganese oxide,

Table VII.—Commercial Analysis of Magnesite.

	Austro-Hungarian.	Grecian.	Indian.	Californian
SiO_2 . .	0·45–5·83	0·20–1·63	0·22–1·17	0·73–7·67
Al_2O_3 . .	0·14–0·48	0·15–0·40	0·10–0·14	0·03–0·26
Fe_2O_3 . .	1·54–7·70	0·08–0·40	0·40–0·65	0·08–0·29
CaO . .	0·20–1·20	0·51–1·68	–0·83	0·04–1·32
MgO . .	39·54–45·00	45·45–47·11	46·28–47·35	44·73–46·61
CO_2 . .	47·99–50·44	49·88–51·77	50·10–51·44	48·08–51·52

phosphoric acid, calcium carbonate, alkalies, and combined water may be present. F. Accum discussed the separation of argillaceous matter from magnesia.

Magnesite is marketed in three forms: (i) *Crude or raw magnesite* as produced at the mine. (ii) *Caustic magnesite* has been calcined at a red heat. It consists mainly of magnesia, and it still retains 2 to 4 per cent. of carbon dioxide. It slakes in contact with water, and combines with magnesium chloride to form Sorel's cement. The calcination of the purer forms of magnesite has at times been effected in retorts so as to obtain the carbon dioxide for making effervescent beverages. (iii) *Dead-burned magnesite* is calcined at as high a temp. as is practicable. It contains less than one per cent. of carbon dioxide. It is hard, dense, and non-plastic and is chemically inert, for it does not slake in air or in water; but it tends to disintegrate when exposed to steam.[5] The shrinkage in making dead-burned magnesite approaches 50 per cent., and the product, if the calcination has been adequately performed, has lost nearly all its shrinking power. It is mainly used for the manufacture of magnesia (*i.e.* magnesite) bricks.

The preparation of normal magnesium carbonate.—T. Bergman,[6] in his essay *De acido aëreo* (Upsala, 1774), described the formation of magnesium carbonate. There is a tendency for magnesium carbonate to separate from its aq. soln. in a hydrated form, or if precipitated it undergoes more or less hydrolysis and appears

as basic carbonate. W. Bramley and W. P. Cochrane heated a soln. of an alkali or ammonium hydro-carbonate or sesqui-carbonate in a closed vessel with magnesia. Hydrated magnesium carbonate is formed, and the hydro- or sesqui-carbonate is converted into normal carbonate. Magnesium carbonate and magnesia alba were found by J. J. Berzelius to contain alkali carbonate and occluded chlorides or sulphates. The alkali carbonate cannot be removed by repeated extraction with boiling water, but W. A. Davis purified the carbonate by dissolving it in water through which carbon dioxide was passing; and decomposing the filtered soln. by boiling. If necessary the treatment is repeated on the washed product. H. de Sénarmont obtained a granular mass of crystals of anhydrous magnesium carbonate by the action of sodium carbonate on magnesium sulphate in a sealed tube between 160° and 175°; he also obtained a similar product from a soln. of magnesium carbonate in carbonic acid at about 155°. R. Marc and A. Simek made anhydrous rhombohedral crystals of magnesite by heating 10 grms. of the precipitated carbonate with 300 c.c. of water and a few grms. of solid carbon dioxide in a sealed tube, in an autoclave at 185° and a press. of 20–30 atm. H. Rose found that if the soln. be evaporated to dryness crystals of magnesite resembling aragonite are produced as well as the basic carbonate—magnesia alba. If this be correct, magnesium carbonate is dimorphous like calcium carbonate. L. Bourgeois found that precipitated magnesium carbonate furnishes crystals of magnesite when heated with urea in a sealed tube at 140°; if ammonium nitrate be used in place of urea, the crystallization does not take place. O. Brill obtained a flocculent form of anhydrous magnesium carbonate by heating the basic carbonate; or precipitation by alkali carbonate from a soln. of a magnesium salt, between 150° and 220°, in an atm. of dry carbon dioxide. C. Heyer proposed to remove the alkali, which adheres very tenaciously to the precipitate, by heating the mass, and then washing out the alkali. A. Röhrig, and J. Treumann heated under press. a soln. of a magnesium salt with calcium carbonate. R. Engel obtained crystals of magnesite by heating ammonium magnesium carbonate, $(NH_4)_2Mg(CO_3)_2.4H_2O$, in a stream of dry air between 130° and 140°. The corresponding potassium salt furnishes a similar result at 200°, and the alkali carbonate can be washed out with cold water.

C. Neuberg and B. Rewald [7] prepared **colloidal magnesium carbonate** by passing a stream of carbon dioxide into a methyl alcohol soln. of magnesium oxide; the opaque liquid clears in about 24 hrs. Water flocculates the colloidal soln.

The physical properties of anhydrous magnesium carbonate.—The natural **crystals** belong to the trigonal system [8] and have the axial ratio $a:c=1:0{\cdot}8095$ with $\alpha=103°\ 21\frac{1}{2}'$. Magnesium carbonate is the first member of a series of isomorphous carbonates, including calcium, manganous, ferrous, zinc, and cadmium carbonates. If G. Rose's statement—*vide supra*—be correct, magnesium carbonate, like calcium carbonate, is dimorphous. A. W. Hull [9] studied the **X-radiogram.** The **specific gravity** has been determined by many observers, and the reported values for crystalline magnesite range from A. Breithaupt's, and R. F. Marchand and T. Scheerer's 3·017, to A. Jentzsch's 3·076. The best representative value approaches 3·037; for amorphous magnesite W. Beck, and R. F. Marchand and T. Scheerer give 2·934; K. Grünberg gives 2·822 for the sp. gr. of magnesium carbonate, and 3·27 for that of ferrous carbonate; and the sp. gr. of isomorphous mixtures of the two changes linearly between these limits. W. Beck's value for the **molecular volume** is 27·38. The **hardness** of crystalline magnesite ranges between $3\frac{1}{2}$ and $4\frac{1}{2}$; amorphous magnesite, with more or less silica, may be still harder than this. This subject has been discussed by A. Reis and L. Zimmermann.

H. Fizeau found the **coefficient of thermal expansion** in the direction of the principal axis to be $\alpha=0{\cdot}00002130$, and in a direction normal to this, $\alpha'=0{\cdot}00000599$. R. Ulrich and E. Wollny found the **specific heat** of magnesite to be 0·2438 between 17° and 99°; and, for artificial magnesium carbonate, 0·2456. A. S. Herschel gave 0·24 for the sp. ht. of magnesite. The **heat of formation,** according to M. Berthelot for the precipitated carbonate (Mg, 3O, C)=266·6 Cals., or $(CO_{2aq.}, MgO_{aq.})=17{\cdot}9$

Cals.; and $K_2CO_{3aq.}+MgSO_{4aq.}=MgCO_3+K_2SO_{4aq.}+2{\cdot}1$ Cals. R. de Forcrand gives $(MgO, CO_2)=28{\cdot}9$ Cals. R. Marc and A. Simek give $-23{\cdot}2$ Cals. for the heat of dissociation of magnesium carbonate. J. Johnston gives for the **free energy** of the dissociation carbonate to oxide 11,700 cals. at 25°. E. Mallard gave for the **index of refraction** of natural crystals for Na-light $\omega=1{\cdot}717$ for the ordinary ray, and $\epsilon=1{\cdot}515$ for the extraordinary ray; the **double refraction** is strongly negative. W. Ortloff's value for the **refraction equivalent** for the ordinary ray is 19·63, and for the extraordinary ray, 14·10, when calculated from Gladstone and Dale's formula. According to P. Bary, magnesite exhibits no fluorescence with **Becquerel's rays** or **Röntgen's rays.** L. Knobloch found the **contact electricity** of powdered magnesite with a plate of platinum, paraffin, or sulphur was negative, and positive with a plate of glass.

The action of heat on magnesium carbonate.—The conclusions drawn by different observers are not always in agreement. H. Rose [10] stated that magnesium carbonate begins to lose carbon dioxide between 200° and 300°, and that when heated to a dull red heat all the carbon dioxide is lost; *au contraire*, R. F. Marchand and T. Scheerer stated that after a prolonged calcination at a bright red heat, the product still retains carbon dioxide. W. C. Anderson found the lowest temp. at which magnesite begins to lose carbon dioxide is 405°; with the so-called heavy carbonate, the temp. is 368°, with light carbonate, 352°, and with crystal carbonate, 271·5°; in the case of light and crystal carbonates, the expulsion of carbon dioxide was stated to be complete at about 750°, while the heavy carbonate retains a little of its carbon dioxide at temp. over 810°. H. le Chatelier found under atm. press. carbon dioxide is given off from magnesite at 680°; and J. A. Hedvall gave 546° for the **dissociation temperature.** K. Friedrich and L. G. Smith found the decomposition of magnesite begins about 570°, and a maximum thermal change in the heating curve occurs at about 600°. A. Vesterberg found that magnesite decomposes more readily than dolomite; that magnesite first gives off carbon dioxide at 448°, and loses virtually all that gas when heated for an hour at 500°, whereas dolomite loses but little if any carbon dioxide at that temp. E. Wülfing also found that the temp. at which magnesite decomposes rapidly is but little over 500°, while with dolomite the temp. is much higher than this. J. Johnston gives for the **dissociation pressure** at 25°, $2{\cdot}6\times10^{-9}$ atm., and for the dissociation temp. 230° at 760 mm.; for the latter, R. Marc and A. Simek give 402°.

O. Brill studied the dissociation of artificial normal magnesium carbonate and, starting with 68·70 grms., he measured the loss in weight after heating 10 mins. at different temp. ranging from 135° to 630°. The following is a selection from a few of his measurements of the weight after heating to different temp.:

	135°	237°	265°	300°	340°	360°	435°	465°	500°	630°
Grms.	68·70	67·90	64·65	64·10	63·45	62·90	59·75	41·10	38·15	32·95

The whole of the results are plotted in Fig. 27. There appears to be a series of breaks in the curve. He considers that this proves that the decomposition of magnesium carbonate takes place in a series of stages corresponding with the formation of a series of basic carbonates each of which has a definite dissociation temp. The carbonates with their dissociation temp. are as follows:—

$10MgO.9CO_2$	$9MgO.8CO_2$	$8MgO.7CO_2$	$7MgO.6CO_2$	$6MgO.5CO_2$	$5MgO.4CO_2$	$7MgO.CO_2$
265°	295°	325°	340°	380°	405°	510°

As W. A. Davis has pointed out, the fact that O. Brill worked with a hygroscopic magnesium carbonate having the composition $MgCO_3.\frac{1}{2}H_2O$, deprives his results of real significance as examples of the dissociation of magnesium carbonate. The presence of water caused the material to break down at 230°, a much lower temp. than that required for the dissociation of magnesite, but approaching the temp. required for the decomposition of the trihydrate. R. Marc and A. Simek also emphasize the fact that precipitated magnesium carbonate retains water very

tenaciously. K. Friedrich and L. G. Smith observed no discontinuities. Accordingly, the breaks are probably due to some cause other than the formation of basic carbonates. Measurements of the dissociation of dried magnesium carbonate are unsatisfactory because of the slowness of the change; the presence of water vapour accelerates the change without disturbing the results because magnesium hydroxide dissociates at 180° at atm. press. The presence of fused potassium nitrate also stimulates the reaction. According to K. Grünberg, when a mixture of artificial magnesite, dolomite, and calcite is heated in a stream of hot air, in a silica vessel, the magnesite is completely decomposed at 410°; the dolomite loses carbon dioxide corresponding with the magnesia content at 500°, and with the lime content at 530°; and finally the calcite is decomposed at 570°. E. Reichardt and T. P. Blumtrill found that 100 grms. of magnesium carbonate absorb 720 c.c. of gas from the air, and the vol. composition of the gas is 64 per cent. nitrogen, 7 per cent. oxygen, and 29 per cent. carbon dioxide.

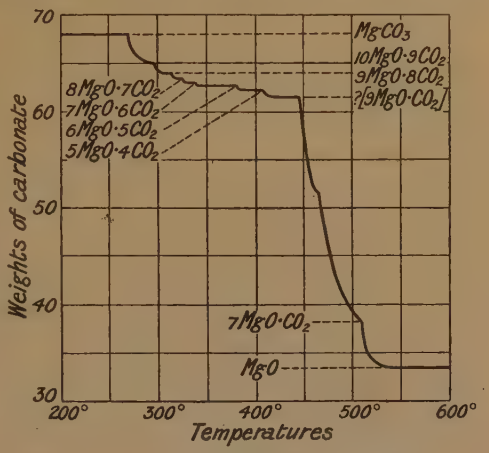

FIG. 27.—The Action of Heat on Magnesium Carbonate.

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§ 15. Hydrated Magnesium Carbonates

Several hydrates of normal magnesium carbonate, $MgCO_3.nH_2O$, have been reported, where n may be 1, 2, 3, $3\frac{3}{4}$, 4, and 5. It is, however, by no means clear if all of them are chemical individuals, and it has been argued that the trihydrate is a hydrated basic hydrocarbonate. H. Beckurts[1] succeeded in making only the trihydrate. It is fairly obvious that the equilibrium relations of the hydrated normal carbonates require examination in the light of the phase rule.

E. A. Nörgaard is the authority for the report of the first two of these hydrates; he claimed to have made **monohydrated magnesium carbonate,** $MgCO_3.H_2O$, as a granular precipitate, by heating a dil. or conc. soln. of magnesium carbonate in carbonic acid, or in a soln. of magnesium sulphate, but not sufficiently high for the evolution of carbon dioxide. He said the precipitate is not changed by washing. The analysis 38·03 per cent. MgO agrees as well with a mixture of $Mg(OH)_2+MgCO_3.3H_2O$ as with $MgCO_3.H_2O$. E. A. Nörgaard made **dihydrated magnesium carbonate,** $MgCO_3.2H_2O$ by precipitation, by adding sodium carbonate to an excess of a soln. of magnesium sulphate—between 18° and 20° the precipitate is amorphous. The temp. falls from 20° to 3·5° during its formation, and rises 3·5° to 5° during its passage to the crystalline state. The analysis 34·06 per cent. MgO agrees with a mixture of $Mg(OH)_2+MgCO_3.3H_2O$ as well as with $MgCO_3.2H_2O$. From the work of W. A. Davis, it is probable that the so-called monohydrated magnesium

carbonate is magnesium hydroxycarbonate, $Mg(HCO_3)(OH)$, and the so-called dihydrated magnesium carbonate is a mixture of anhydrous magnesium hydroxycarbonate and of its dihydrate, $Mg(HCO_3)OH.2H_2O$. According to T. C. W. Bröksmit, the amorphous precipitate obtained by adding sodium, potassium, or ammonium carbonate, or hydrocarbonate to a soln. of magnesium sulphate, and generally supposed to be a basic carbonate, becomes crystalline after some time, and may be trihydrated magnesium carbonate, $MgCO_3.3H_2O$.

The rare mineral *nesquehonite*, **trihydrated magnesium carbonate,** $MgCO_3.3H_2O$, was discovered in the anthracite mine of Nesquehoning, Lansford, Pa., and described by F. A. Genth and S. L. Penfield (1890). The mineral was first observed as being formed as stalactites in one of the galleries. It was also found by G. Friedel at Isère (France), and by H. Leitmeier as a deposit from the mineral springs at Rohitsch-Sauerbrunn (Unterstiermark) at about 6°. According to J. J. Berzelius, the trihydrate is formed when a soln. of magnesium carbonate in aq. carbonic acid is allowed to evaporate spontaneously in air ; or, according to J. Fritzsche, when the soln. sat. with carbon dioxide under press. is kept above 20°—the Salzbergwerk Neu-Stassfurt has a number of patents involving modifications of these processes. H. Leitmeier found the soln. furnishes the basic carbonate, $Mg_4C_3O_{10}.6H_2O$, from the b.p. down to 60°–65° ; from 60°–55°, the basic carbonate is mixed with the trihydrate, $MgCO_3.3H_2O$; at still lower temp. the trihydrate forms alone ; and below 10°, the pentahydrate, $MgCO_3.5H_2O$, appears. C. Kippenberger found that crystals of his $MgCO_3.3\frac{3}{4}H_2O$ form the trihydrate when allowed to stand in dry air, or over sulphuric acid. J. Fritzsche observed that the pentahydrate loses two-fifths of its water and forms the trihydrate when exposed in a glass tube to sunlight ; and when treated in other ways—*vide infra.* According to A. F. de Fourcroy, and V. Rose, a mixture of aq. soln. of magnesium sulphate and sodium or potassium hydrocarbonate is initially clear, but it deposits crystals of the trihydrate when allowed to stand for some time ; according to J. B. J. D. Boussingault, sodium sesquicarbonate can be used in place of the hydrocarbonate. Again, J. Fritzsche, E. Soubeiran, and P. A. Favre found that the precipitate which normal sodium carbonate gives with a soln. of magnesium sulphate is converted into crystals of the trihydrate if allowed to stand for a few days at a temp. between 0° and 10°—E. A. Nörgaard added that it is best to use an excess of magnesium sulphate, and if the temp. is below 22°, the pentahydrate is formed. According to a patent of the Salzbergwerk Neu-Stassfurt, a soln. of potassium magnesium carbonate reacts with magnesia : $2(MgCO_3.KHCO_3.4H_2O)+MgO=K_2CO_3+3(MgCO_3.3H_2O)$ at temp. between 20° and 50°.

According to W. A. Davis, the salt which is supposed to be the trihydrated normal carbonate is really a *dihydrated magnesium hydroxycarbonate,*

$$Mg<^{OH}_{HCO_3}.2H_2O$$

This opinion is based on the fact that the salt loses only two-thirds of its water when heated at 100° in a current of air, or boiled with a liquid like xylene (b.p. 137°) ; the remaining third of the water is expelled only at a much higher temp., and always together with some carbon dioxide.

W. A. Davis prepared dihydrated magnesium hydroxycarbonate, the so-called trihydrated magnesium carbonate, by mixing cold soln. of eq. quantities of sodium carbonate and magnesium sulphate, each dissolved in 15 parts of water. The precipitate first formed was left in contact with the mother liquor when it became entirely crystalline. The mother liquid, after standing for three months, had deposited a further crop of needle-like crystals. In both cases, the crystals had the composition $Mg(HCO_3)OH.2H_2O$. The conversion of the dihydrate into the anhydrous salt, $Mg(HCO_3)OH$, is effected as previously indicated.

The mode of formation of this salt shows that a basic carbonate cannot be produced by the decomposition of the hydroxyhydrocarbonate by water at the ordinary temp. ; the crystals separated from the mother liquor remained in contact with water containing a slight excess of alkaline carbonate during three months,

and yet contained magnesia and carbon dioxide in the ratio corresponding with a normal carbonate. Water, free from alkali, is practically without action on magnesium hydroxyhydrocarbonate at ordinary temp. W. A. Davis supposes that the formation of the hydroxyhydrocarbonate in a soln. of magnesium carbonate in carbonic acid, when the partial press. of the carbon dioxide is low enough, is due to hydrolysis: $Mg(HCO_3)_2+H_2O=Mg(OH)(HCO_3)+H_2CO_3$. When this compound is boiled with water, two actions take place simultaneously: $Mg(HCO_3)OH.2H_2O=Mg(HCO_3)OH+2H_2O$; and $Mg(HCO_3)OH+H_2O=Mg(OH)_2+H_2O+CO_2$, so that the product is a mixture of magnesium hydroxide and hydroxycarbonate. The change is slow because a coating of magnesium hydroxide protects the interior of the crystals from the water.

Needle-like **crystals** of the trihydrate were obtained by W. A. Davis. According to F. A. Genth and S. L. Penfield, the natural salt belongs to the rhombic system with axial ratios $a:b:c=0{\cdot}6450:1:0{\cdot}4568$; and their values for the **specific gravity** of nesquehonite range from 1·83 to 1·852; H. Leitmeier gave 1·854; and for the artificial crystals, G. von Knorre gave 1·808, and H. Beckurts, 1·875. Well-developed crystals of magnesite are rare. R. W. G. Wyckoff tried to get Laue's patterns with some short six-sided prisms, but the results were not satisfactory. **X-radiograms** of the powder by W. P. Davey and E. O. Hoffman showed that the space lattice is like that of sodium chloride. A. W. Hull also studied the subject. According to F. A. Genth and S. L. Penfield, the **hardness** of the mineral is $2\frac{1}{2}$; and the **indices of refraction** for Na-light are $\mu_\alpha=1{\cdot}495$, $\mu_\beta=1{\cdot}501$, and $\mu_\gamma=1{\cdot}526$. P. Pascal gave 727×10^{-7} for the mol. **coefficient of magnetization.**

J. Fritzsche said the crystals are stable in air; and J. J. Berzelius said the crystals effloresce in dry air. Observations on the solubility of the salt are indicated below. The crystals were found by E. Soubeiran to have an alkaline taste, and to colour a decoction of violets green. H. Beckurts said the salt loses 15·27 per cent. of water and carbon dioxide at 100°—H. Rose assumed that water alone was lost at this temp.—at 200° more water and carbon dioxide are given off; and at 300°, all these gases have not been driven off; but all can be driven off at a higher temp. leaving residual magnesium oxide. J. J. Berzelius, and E. Soubeiran found the soln. gives off carbon dioxide when boiled, and deposits *magnesia alba;* H. Rose also noted the loss of carbon dioxide when the soln. is boiled, although J. Fritzsche found boiling water did not decompose the salt. J. J. Berzelius, and A. Bineau observed that when cold water dissolves the trihydrate a basic salt is precipitated and an acid salt remains in soln. According to V. A. Jacquelain, the salt loses carbon dioxide in a stream of moist air, or at 90° or 100° in a stream of water vapour.

C. Kippenberger prepared what he regarded as **pentadecatetritahydrated magnesium carbonate,** $MgCO_3.3\frac{3}{4}H_2O$, by dissolving freshly precipitated magnesium carbonate in an aq. soln. of potassium or sodium hydrocarbonate, and allowing the soln. to stand for some time. The crystals are said to pass readily into the trihydrate, on standing in dry air, or over sulphuric acid. J. C. G. de Marignac obtained fine prismatic crystals of **tetrahydrated magnesium carbonate,** $MgCO_3.4H_2O$, by very slowly evaporating a soln. of magnesium hydrocarbonate. The crystals belong to the monoclinic system, and have the axial ratios $a:b:c=1{\cdot}6366:1:0{\cdot}9653$, and $\beta=101°\ 33'$. A. Damour obtained the same product, but E. A. Nörgaard supposed it to be a mixture and not a chemical individual, even though J. C. G. de Marignac's analysis of an isolated crystal gave numbers in agreement with $MgCO_3.4H_2O$.

J. Fritzsche found that when a sat. soln. of magnesium carbonate in carbonic acid is exposed to the cold of winter in a loosely covered vessel, a mixture of tri- and **pentahydrated magnesium carbonate,** $MgCO_3.5H_2O$, is formed, and the proportion of the higher hydrate increases the lower the temp. of formation. E. A. Nörgaard prepared the pentahydrate by adding normal sodium carbonate to a soln. of magnesium sulphate at 0° until it begins to appear turbid, and allowing the mixture to stand for some time. G. Moressée dissolved magnesium oxide in water at 10°, sat. with carbon dioxide under a press. of 5–6 atm. The filtrate deposits

monoclinic crystals of the pentahydrate ; the analyses sometimes show a somewhat higher percentage of magnesia, presumably owing to a partial decomposition.

The mineral *lansfordite* was reported by F. A. Genth and S. L. Penfield, from the anthracite mines of Nesquehoning, Lansford, Pa., where it has probably been formed by the percolation of ground waters rich in magnesia and carbon dioxide. Lansfordite occurs in prismatic crystals which were stated to belong to the triclinic system, the axial ratios being $a:b:c=0{\cdot}5493:1:0{\cdot}5655$. The chemical analysis corresponds with $3MgCO_3.Mg(OH)_2.21H_2O$. H. J. Brooke gave for the axial ratios of the monoclinic tabular crystals of the pentahydrate $a:b:c=1{\cdot}1156:1:1{\cdot}7817$, and $\beta=107°\ 40'$, but there appears to be some mistake here. The crystals of the pentahydrate obtained by G. Moressée were found by G. Cesaro to be hexagonal prisms belonging to the monoclinic system with axial ratios $a:b:c=1{\cdot}6393:1:0{\cdot}96676$, and $\beta=77°\ 50'\ 58''$; and the latter claimed that the crystalline form of the pentahydrate is identical with that of lansfordite, and that the smaller proportion of carbon dioxide in the analysis of lansfordite is really due to the decomposition of the unstable mineral during analysis. The sp. gr. of lansfordite was found to vary from 1·692 to 1·540 ; H. Leitmeier gave 1·688, and he also concluded that lansfordite is really partially decomposed pentahydrated magnesium carbonate, and that the crystallographic data of F. A. Genth and S. L. Penfield were defective owing to the imperfections in the specimen available for measurement. G. Cesaro gave 1·73 (19°) for the sp. gr. of the pentahydrate, and he stated that the crystals are harder than gypsum, but softer than calcite ; F. A. Genth and S. L. Penfield gave $2\frac{1}{2}$ for the hardness of lansfordite.

According to E. A. Nörgaard, there are two forms of the pentahydrate—tabular and columnar. The former is produced below 16°, the latter below 10°. J. Fritzsche found the crystals of the pentahydrate part with two-fifths of their combined water when exposed to air, and more rapidly on exposure to sunlight ; the same result is obtained by keeping the pentahydrate for a long time in water at 50° ; and when heated to 75°, they lose carbon dioxide as well as water. E. A. Nörgaard said that the tabular crystals pass into the trihydrate if heated under water at 20°–25°; and when warmed under water to about 100°, they begin to lose carbon dioxide provided contact with the walls of the vessel is avoided ; if the temp. be raised slowly, the pentahydrate swells at about 50°, and passes into the trihydrate ; if the temp. be raised very rapidly to 90°, the tabular crystals pass into the monohydrate. The columnar crystals effloresce on exposure to air, and decompose when boiled in water more readily than the tabular crystals. The solubility of the pentahydrate is indicated in the next section. According to G. Cesaro, the aq. soln. is alkaline to litmus and phenolphthalein, and he found that the residue obtained by the spontaneous evaporation of its aq. soln. seems to contain both the original substance and a small quantity of nesquehonite, $MgCO_3.3H_2O$. A soln. of G. Moressée's carbonate becomes turbid when heated to boiling, but the precipitate redissolves on cooling the liquid to 10°, and the latter, when evaporated, leaves an amorphous residue containing crystals of both $MgCO_3$, $5H_2O$ and of nesquehonite. H. Leitmeier found the heating curve of the pentahydrate to show a well-defined break at about 50° corresponding with its transformation into the trihydrate. The tetrahydrate of J. C. G. de Marignac gives no such break.

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§ 16. The Solubility of Magnesium Carbonate

The available data for the solubility of normal magnesium carbonate in *water* are not satisfactory. T. Bergman[1] made some observations on this subject in 1775. P. Butini found that "an ounce of distilled water dissolves from 1·0 to 1·5 grains of magnesia, whereas the same quantity of aërated water takes up 13 grains." According to A. M. Pleischl, and M. Pichard, when powdered magnesite is moistened with water, it gives an alkaline reaction with vegetable colouring matters. N. Ljubavin reported that at 26°, 100 grms. of water dissolve 0·27 grm. of normal magnesium carbonate, and 8·12 grms. of trihydrated magnesium carbonate, $MgCO_3.3H_2O$; on the other hand, W. A. Davis stated that magnesite and dolomite are as resistant to the solvent action of water as is calcium carbonate. Magnesite is insoluble in water, and is not affected to an appreciable extent by boiling it with water or with an aq. soln. of an alkali carbonate. F. Gothe says water free from carbon dioxide dissolves 94·4 mgrms. of magnesium carbonate per litre; and R. C. Wells, that a soln. of distilled water in equilibrium with atm. air, at 20°, dissolves 0·083 mgrm. of magnesite. The diversity of the data indicated below has been explained by assuming the existence of various modifications of magnesium carbonate which slowly pass into stable forms.

The anhydrous magnesium carbonate prepared by R. Engel by heating to 130° double ammonium magnesium carbonate, is sensitive towards water, for it slakes in moist air, and readily forms the trihydrate, $MgCO_3.3H_2O$; 100 c.c. of water was also found to dissolve 0·2 grm. of the carbonate. According to E. A. Nörgaard, 100 parts of water, between 0° and 7°, dissolve about 0·167 part of both forms of the pentahydrate, $MgCO_3.5H_2O$; and, according to G. Cesaro, 100 parts of cold water dissolve 0·374 of the pentahydrate prepared by G. Moressée. A. Bineau, R. Engel, and H. Beckurts noted the solubility of the trihydrate, $MgCO_3.3H_2O$, in water, and E. A. Nörgaard found that 100 grms. of soln. between 0° and 16°, contained:

	0°	6·5°	8°	16°	15°	25°	35°
$MgCO_3.3H_2O$.	0·15	0·153	0·155	0·179;	0·141	0·129	0·105 grm.

The data between 15° and 35° are by F. Auerbach. F. Kohlrausch and F. Rose did not get constant results by measuring the conductivity of sat. soln., but later F. Kohlrausch obtained 794×10^{-6} rec. ohms for the sp. conductivity of a soln. sat. at 18°. According to E. Soubeiran, when an aq. soln. of magnesium carbonate is boiled, carbon dioxide is evolved, and *magnesia alba* is precipitated. A. Cavazzi showed that while the dissociation of calcium carbonate in boiling water is limited when a certain proportion of calcium hydroxide has been dissolved, no limit occurs with the dissociation of magnesium carbonate under these conditions—magnesium hydroxide is a weak base nearly insoluble in water, while calcium hydroxide is a strong base fairly soluble in water; the former, too, has little affinity for carbon dioxide, while the latter has a strong affinity for that gas.

N. Ljubavin observed that the solubility of magnesium carbonate in water is augmented by the presence of *calcium chloride*, or of *sodium chloride*. R. C. Wells also studied the solubility of magnesium carbonate in natural waters. E. Fleischer

found an aq. soln. of *calcium sulphate* readily decomposes magnesium carbonate, particularly if some sodium chloride is present. According to F. K. Cameron and A. Seidell, in air free from carbon dioxide, the solubility of magnesium carbonate increases to a maximum and then decreases with increasing conc. of sodium chloride ; thus, expressing the results in grams per litre, at 23°,

NaCl . .	0·0	28·0	59·5	106·3	147·4	231·1	272·9	331·4
$MgCO_3$ . .	0·176	0·418	0·527	0·585	0·544	0·460	0·393	0·293

but, when in contact with an atm. of carbon dioxide, under normal press., the solubility of magnesium carbonate decreases regularly with increasing conc. of sodium chloride.

NaCl .	7·0	56·5	119·7	163·9	224·8	306·6
$MgCO_3$.	30·64	30·18	27·88	24·96	20·78	10·75

F. K. Cameron and A. Seidell added : " This appears to be a real exception to the hypothesis of electrolytic dissociation for which no explanation based upon that hypothesis can be offered." C. Kippenberger explains the phenomenon by assuming that the products of a reaction between the two salts suffer hydrolysis. The solubility of magnesium carbonate in soln. of *sodium sulphate*, at 24°, has been measured by F. K. Cameron and A. Seidell. In an atm. free from carbon dioxide, the solubility increases with increasing conc. of sodium sulphate :

Na_2SO_4 . .	0·00	25·12	54·76	95·68	160·8	191·9	254·6	305·1
$MgCO_3$ . .	0·216	0·586	0·828	1·020	1·230	1·280	1·338	1·388

The solubilities at 35·5° are less, showing that the solubility of magnesium carbonate in soln. of sodium sulphate, with soln. exposed to an atm. of carbon dioxide, under normal press., increases slightly and then decreases with increasing conc. of sodium sulphate. W. A. Davis found the presence of *potassium sulphate*, *potassium nitrate*, or *potassium chloride* favours the soln. of magnesium carbonate, and he believes the increased solubility is due to the formation of mixed salts, $KSO_4.Mg.CO_3K$; $NO_3.Mg.KCO_3$; $Cl.Mg.KCO_3$, etc. According to F. Gothe, the solubility of magnesium carbonate is increased by the presence of *alkali chlorides*, *nitrates*, *and sulphates* in the water, but decreased by *alkali carbonates*, and by the *alkaline earth chlorides*, *nitrates*, *and sulphates ; ammonium salts* decompose the carbonate and the effect on the solubility cannot be determined. The solubility is increased when the water contains *organic* (*humus*) *substances*, especially when alkali salts are also present, but is decreased in the presence of alkali-earth salts. According to R. C. Wells, certain natural waters, freely exposed to the atm., seem to be supersaturated with respect to magnesite, but none of them approaches very closely to the point of sat. of the trihydrate. A. Frébault and A. Destrem have studied the action of *disodium hydrophosphate* on magnesium carbonate. G. C. Wittstein found magnesium carbonate is readily soluble in cold soln. of the *alkali borates*, and when heated, the soln. forms a precipitate which redissolves on cooling.

Freshly precipitated magnesium carbonate is soluble in soln. of *magnesium chloride* or *magnesium sulphate*. According to E. A. Nörgaard, the solubility of magnesium carbonate is raised in the presence of magnesium sulphate, and with a mol of the latter salt per litre,

	0°	10°	20°	30°
$MgCO_3$ . . .	0·20	0·15	0·11	0·18 mol.

T. S. Hunt was able to dissolve 5 grms. of magnesium carbonate in a litre of water containing 60 grms. of heptahydrated magnesium sulphate and a little sodium chloride ; when the alkaline soln. is heated a precipitate is formed which redissolves as the soln. cools. According to E. A. Nörgaard, freshly prepared tabular crystals of pentahydrated magnesium carbonate, dissolve in a 4 per cent. soln. of magnesium

sulphate or sodium carbonate, but the prismatic form is insoluble in these menstrua. W. A. Davis supposes a mixed salt of the type $Mg<^{SO_4}_{CO_3}>Mg$ is formed.

According to C. Kippenberger, soln. of *sodium carbonate* readily dissolve freshly precipitated magnesium carbonate. F. K. Cameron and A. Seidell found for soln. in equilibrium with an atm. free from carbon dioxide at 25°, when the results are expressed in grams per litre,

Na_2CO_3 . .	0·00	23·12	50·75	86·42	127·3	160·8	181·9	213·2
$MgCO_3$ . .	0·223	0·288	0·510	0·879	1·314	1·636	1·972	2·317

Except for the lower conc., the increase in solubility of the magnesium carbonate with increase in the amount of sodium carbonate is represented by an approximately straight line. The sp. gr. of the soln. were also determined. F. Auerbach found at 15°, 25°, and 35° for soln. of *potassium hydrocarbonate*, when the results are expressed in mols per litre, at 25°:

$KHCO_3$ . .	0	0·0985	0·2210	0·3434	0·4985	0·3906	0·5893	0·6406	1·125
$MgCO_3$ . .	0·0087	0·0115	0·0149	0·0181	0·0217	0·0196	0·0128	0·0117	0·0061
Solid phases .	$MgCO_3.3H_2O$					$MgCO_3.KHCO_3.4H_2O$			

The solubility thus increases as the conc. of the alkali hydrocarbonate increases until the double salt, $MgCO_3.KHCO_3.4H_2O$, is formed, and thereafter the solubility diminishes. The solubility of *magnesia alba* was found by P. Butini,[2] T. Bergman, C. L. Berthollet, and F. Gothe to be raised by the presence of *carbon dioxide* in soln. A similar remark applies to magnesium carbonate.

P. Butini stated that water may be over-saturated with magnesia and yet pass through the filter-paper and remain clear; such a soln. is obtained by immediately filtering the water in which epsom salt has been decomposed; and if heated to 20° (which may be done in the palm of the hand), it lets fall its earth, which is redissolved when the liquid cools to about 15°. This is a very amusing experiment.

According to E. Soubeiran, the sat. soln. contains twice as much carbon dioxide as the normal carbonate. It was assumed by A. Cossa, C. Kippenberger, etc., that **magnesium hydrocarbonate,** $Mg(HCO_3)_2$, is formed, but the salt has not been isolated; and, according to F. P. Treadwell and M. Reuter, the hydrocarbonate exists in aq. soln. only in the presence of a large excess of carbon dioxide; if the partial press. of this gas falls below 2 per cent., the soln. loses all its free carbon dioxide and part of that present as hydrocarbonate. At 15°, a litre of a soln. is estimated to contain 1·9540 grms. of hydrocarbonate, and 0·7156 grm. of carbonate. The conclusion is supported by R. Rinne; and P. N. Raikow found that a soln. of magnesium nitrate precipitated by a definite amount of potassium hydroxide, absorbed enough carbon dioxide to form the hydrocarbonate. M. Monhaupt tried to precipitate the hydrocarbonate by adding alcohol to the sat. soln., but he obtained only the trihydrated carbonate, $MgCO_3.3H_2O$. W. A. Davis also found that the solid phase which separated from a soln. of the so-called hydrocarbonate is trihydrated magnesium carbonate, a result confirmed by F. K. Cameron and W. O. Robinson. The latter also measured the vap. press. of carbon dioxide, expressed in p cms. of mercury, when w grms. of carbon dioxide are successively added to wet magnesium hydroxide:

w . .	0·00	0·1519	0·1953	0·2170	0·3038	0·3255	0·3906	0·5642
p . .	76	78	80	88	90	112	142	275

The results are plotted in Fig. 28, which shows a curve consisting of three parts. The portion AB remains constant, and it corresponds with the formation of normal magnesium carbonate; the portion BC corresponds with the absorption of carbon dioxide—some of the solid phase appeared to pass into soln.; and the portion CD in which the addition of carbon dioxide has no influence on the solid phase. When the excess of carbon dioxide is allowed to escape until p has reached atm. press..

the molar ratio $MgO : CO_2$ in the solid is nearly that required for the hydrocarbonate. F. K. Cameron and W. O. Robinson regard the solid as a soln. of carbon dioxide in trihydrated magnesium carbonate. The soln. of magnesium carbonate in carbonic acid containing "13 grains per ounce" is the *fluid magnesia* or the *liquor magnesiæ carbonates* of the British Pharmacopœia.

H. Leitmeier found a litre of water sat. with carbon dioxide at ordinary temp. dissolves 0·08 grm. of crystalline magnesite, and 0·22 grm. of amorphous magnesite. The solubility of magnesium carbonate in aq. soln. of carbon dioxide depends on the slowness of the conversion of one modification into another—say, the basic carbonate into trihydrated normal carbonate—and this, in turn, depends on the source of the solid employed, and on the time of contact. Thus, R. Engel found the following values for the solubilities starting with different materials, and after the elapse of different periods of time :

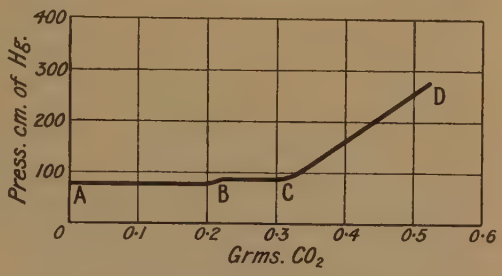

FIG. 28.—Pressure of Carbon Dioxide over Magnesium Hydroxide.

Time in hrs.	Magnesium oxide.	Trihydrated normal carbonate.	Hydrocarbonate.
0·15	3·5	4·3	1·25
1·00	6·4	6·4	2·50
1·30	6·4	6·4	3·75
9·00	6·4	6·4	5·00

Before the importance of this was recognized, the results were very discordant; thus, a litre of water sat. with carbon dioxide was found by J. R. von Wagner, and G. Merkel to dissolve 1·31 grms. of magnesium carbonate; H. Beckurts, 8·39 grms.; and A. Bineau, 23·3 grms. R. Engel and J. Ville give for the solubility of magnesium carbonate, in grams per litre, in water at 19·5°, sat. with carbon dioxide at various press. expressed in atm. :

CO_2 . .	1	2·1	3·2	4·7	5·6	6·2	7·5	9·0 atm.
$MgCO_3$ . .	25·79	33·11	37·30	43·50	45·20	48·50	51·20	56·59

They also gave for the solubility of magnesium carbonate in water sat. with carbon dioxide at various temp. at a press. of one atm., when the results are expressed in grams per litre :

	13·4°	19·5°	29·3°	46·0°	62·0°	70·0°	82·0°	90°	100°
$MgCO_3$ . .	28·45	25·79	21·95	15·7	10·35	8·1	4·9	2·4	0·0

T. Schlösing represented the solubility of magnesium carbonate in water at different press. p of carbon dioxide, by the empirical formula $p^{0·362}=0·0398y$, where y denotes the amount of magnesium hydrocarbonate in the soln. expressed in grams per litre. R. Engel obtained good results with the empirical formula $p^{0·333}=0·814y$, *i.e.* with $y=1·934\sqrt[3]{p}$, or, at a definite temp., the quantity of magnesium carbonate dissolved by water with carbon dioxide in soln., is proportional to the cube root of the press. of the carbon dioxide.

G. Bodländer attempted to obtain a formula of the same form as that employed to represent the solubility of calcium carbonate in water containing carbon dioxide, but he found it necessary to assume the presence of ions in soln. of the form $\{(MgCO_3)_n.MgOH\}^{\cdot}$. F. P. Treadwell and M. Reuter have also shown that, at the lower conc., there is less carbon dioxide in soln. than corresponds with the formula $Mg(HCO_3)_2$, a conclusion which was confirmed by R. Rinne. In the opinion of J. Johnston, the results of F. P. Treadwell and M. Reuter, and of J. W. Leather and J. N. Sen on the ternary system, $MgCO_3—H_2CO_3—H_2O$, and the quaternary system, $CaCO_3—MgCO_3—H_2CO_3—H_2O$, are vitiated by defective analyses or by the

uncertainty whether equilibrium was really attained. J. Johnston calculated the **solubility product,** at 18°, to be $[Mg^{\cdot\cdot}][CO_3'']=1{\cdot}2\times10^{-4}$, or else $[Mg^{\cdot\cdot}][OH']^2=1{\cdot}2\times10^{-11}$.

According to J. Johnston, (1), $[Mg^{\cdot\cdot}][CO_3'']=K$; (2), $[H_2CO_3]=k'[CO_2]=c'p$, where p is the partial press. of the carbon dioxide; (3), $[H^{\cdot}][HCO_3']=k_1[H_2CO_3]$; (4), $[H^{\cdot}][CO_3'']=k_2[HCO_3']$; (5), $[H_2CO_3]=nk[CO_2]=ncp$, where $c=a/22{\cdot}4$, and n, from the work of J. Walker and W. Cormack on the proportion of the total carbon dioxide in soln. existing as H_2CO_3, is greater than 0·5. By dividing (3) by (4), it follows (6), $[HCO_3']^2/[CO_3''][H_2CO_3]=k_1/k_2=r$; and when combined with (5), there remains (7), $[HCO_3']^2/[CO_3'']cp=nr$. Consequently, (8), $[Mg^{\cdot\cdot}][HCO_3']^2=nrKcp$, or $nrK=[Mg^{\cdot\cdot}][HCO_3']^2/cp$; (9), $[OH']/[HCO_3']=K_\omega/nk_1cp$, where K_ω is the constant for water; (10), $[OH']^2/[CO_3'']=K_\omega^2/nr_1K_2cp$. At 18°, for partial press. ranging from 0·0002 to 0·0005 atm., J. Johnston calculated from R. Engel's measurements (7), $nrcp=229{\cdot}6p$; (8), $nrKcp=2{\cdot}755\times10^{-2}p$; (9), $K_\omega/nk_1cp=4{\cdot}012\times10^{-7}p$; (10), $K_\omega^2/nk_1k_2cp=3{\cdot}694\times10^{-11}p$; and either (11), $[Mg^{\cdot\cdot}][CO_3'']=K=1{\cdot}2\times10^{-4}$; or (12), $[Mg^{\cdot\cdot}][OH']^2=1{\cdot}2\times10^{-11}$. By combining (1) and (10), or (8) and (9), it follows that at 18° $[Mg^{\cdot\cdot}][OH']^2=4{\cdot}433\times10^{-15}/p$, a value which exceeds (12) when p is less than 0·000369.

When $p<0{\cdot}000369$, at 18°, the solid phase is not $MgCO_3.3H_2O$, but $Mg(OH)_2$. At the transition press. 0·000369, both solid phases are in equilibrium. If the press. of the carbon dioxide is kept constant at p atm., and water be evaporated from the soln. so slowly at 18° that equilibrium conditions are continuously maintained, the following amounts of magnesium hydroxide, or trihydrated carbonate, will be obtained (grams per litre):

p . . .	0	0·00030	0·00030	0·00035	0·00040	0·00045	0·00050 atm.
Total [Mg] .	0·00015	0·01934	0·02486	0·02742	0·02868	0·02924	0·02976 mols
Grms. . .	0·0087	1·13	1·45	1·60	3·97	4·05	4·12
		$Mg(OH)_2$			$MgCO_3.3H_2O$		

The transition press. increases rapidly with temp. because K_ω^2/nk_1k_2 increases rapidly whilst K/c varies but little; the increase cannot be calculated because the rate of change of k_2 with temp. is not known.

It follows, adds J. Johnston, that the ordinary methods of preparing magnesium carbonate (in which, it is safe to say, a state of equilibrium is not attained continuously) will yield a product contaminated with hydroxide, the amount of which will depend upon the mode of working generally, and upon the prevailing partial press. of CO_2 over the liquid in particular; moreover, that this contamination can be avoided completely by working with a partial press. p greater than a certain limit.

J. Johnston continues: In soln. sat. with both calcium and magnesium carbonates, the ratio of the conc. of $Mg^{\cdot\cdot}$ and $Ca^{\cdot\cdot}$ must have a definite value; thus, at 16°

$$\frac{[Mg^{\cdot\cdot}]}{[Ca^{\cdot\cdot}]}=\frac{[Mg^{\cdot\cdot}][CO_3'']}{[Ca^{\cdot\cdot}][CO_3'']}=\frac{K_{Mg}}{K_{Ca}}=\frac{1{\cdot}4\times10^{-4}}{1\times10^{-8}}=14{,}000$$

Hence, if a soln. of the two carbonates in carbonic acid is evaporated, or if the partial press. of the carbon dioxide be gradually reduced, at 16°, calcium carbonate will be precipitated so long as the above ratio is less than 14,000, as would normally be the case in natural waters when the press. of the carbon dioxide is sufficient to prevent the precipitation of magnesium hydroxide. The order of precipitation will be reversed if the relative conc. of the magnesium ions be greater than 14,000, as could be the case when a soluble magnesium salt is present. These deductions are valid when $CaCO_3$ and $MgCO_3.3H_2O$ are the only solid phases which separate; if a solid soln. of the two be formed at certain conc., these deductions would have to be modified accordingly. If the partial press. of carbon dioxide is such that magnesium hydroxide may precipitate, it follows that:

$$\frac{[Mg^{\cdot\cdot}]}{[Ca^{\cdot\cdot}]}=\frac{[Mg^{\cdot\cdot}][OH']^2}{[Ca^{\cdot\cdot}][OH']^2}=\frac{1{\cdot}2\times10^{-11}p}{3{\cdot}43\times10^{-19}}=3{\cdot}5\times10^{7}p$$

a ratio which decreases steadily as p is reduced. Hence calcium carbonate precipi-

tated from a soln. containing magnesium may be very readily contaminated with appreciable proportions of magnesium hydroxide, which would be removed only slowly by repeated re-precipitations. J. C. Hostetter, for example, has emphasized how difficult it is to get calcium carbonate free from magnesia. This difficulty may be obviated very easily, namely, by conducting the operations in such a way that the liquid is always sat. with CO_2 at a press. above a certain limiting value; this limit, which increases with the temp., cannot at present be specified very accurately, but is in all probability not greater than 1 atm. for any conditions likely to be encountered in actual practice.

According to C. L. Berthollet, the soln. of magnesium carbonate has a bitter taste, and an alkaline reaction, and C. H. Pfaff, A. M. Pleischl, and C. L. Berthollet stated that the alkalinity towards vegetable colouring matters—tincture of logwood, tumeric, red litmus, etc.—is maintained even when a great excess of carbon dioxide is in soln., but, according to the last-named, the soln. gives a green colour with tincture of violets, and he also stated that the soln. becomes turbid when heated to 75°, but recovers its transparency on cooling. According to J. J. Berzelius, and J. Fritzsche, when the soln. is heated to 50°, or, according to E. Soubeiran, when evaporated in vacuo, trihydrated normal carbonate, $MgCO_3.3H_2O$, is deposited. According to W. Weldon, and E. Bohlig, when sodium chloride is added to a sat. soln. of magnesium carbonate and carbon dioxide, sodium hydrocarbonate is precipitated, and magnesium chloride remains in soln.

Magnesite is not quickly attacked by cold *hydrochloric acid* or *sulphuric acid*, but it dissolves readily in the warm acids. According to K. Haushofer, and A. Vesterberg, compact magnesite is more quickly dissolved by *acetic acid* than crystallized magnesite; and the solubility of crystallized magnesite decreases with increasing conc. of the acid. A. Vesterberg, and T. S. Hunt found that magnesite dissolves more slowly than dolomite in acetic acid; K. Haushofer came to the opposite conclusion. F. W. Pfaff found that powdered magnesite is very slightly soluble in a soln. of *hydrogen sulphide* in water; and its solubility in an aq. soln. of *ammonium sulphide* is small. L. Naudin and F. de Montholon have studied the action of hydrogen sulphide on magnesite suspended in water. J. A. Hedvall and J. Heuberger found the reaction temp. and the thermal value of the reaction between magnesium carbonate and *calcium oxide* to be respectively 300° and 2·5 Cals.; with *strontium oxide*, 240° and 11·5 Cals.; and with *barium oxide*, 230° and 19 Cals.

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§ 17. The Basic Magnesium Carbonates—Magnesium Oxycarbonates

A considerable number of distinct basic magnesium carbonates have been reported :

Representing the proportions of $MgO : CO_2 : H_2O$ by numerals in that order, J. Fritzsche [1] prepared the (1), 3 : 2 : 3-carbonate ; also the (2), 4 : 3 : 4-carbonate ; H. Rose the (3), 4 : 3 : 7-carbonate ; J. J. Berzelius, the (4), 4 : 3 : 8-carbonate ; J. Fritzsche and H. Rose, the (5), 5 : 4 : 5-carbonate ; H. Rose, the (6), 5 : 4 : 6-, (7), 5 : 4 : 7-, (8), 5 : 4 : 8-, and (9), 5 : 4 : 9-carbonates ; H. Rose, and V. A. Jacquelain (10), 5 : 4 : 10-carbonate ; H. Rose (11), 5 : 4 : 11-, and (12), 5 : 4 : 12-carbonate ; G. Kittel (13), 5 : 4 : 16-carbonate ; H. Beckurts (14), 7 : 5 : 9 ; H. Rose (15), 6 : 4 : 6-carbonate, and V. A. Jacquelain (16), 6 : 5 : 14-carbonate. There are also the native basic carbonates 2 : 1 : 3 ; 2 : 1 : 4 ; 4 : 3 : 3 ; and 4 : 3 : 4 ; and the anhydrous basic carbonates. With $MgO : CO_2$, *viz.* 10 : 9 ; 9 : 8 ; 8 : 7 ; 7 : 6 ; 6 : 5 ; 5 : 4 ; and 9 : 7-carbonates.

This confusing variety of the basic magnesium carbonates is usually regarded as a consequence of the more or less incomplete hydrolysis of the normal carbonate ; and this view can be traced back to H. Rose's work in 1851–2, *Ueber den Einfluss des Wassers bei chemischen Zersetzungen*, whereby it was shown that water acting as a weak acid is able to decompose more or less completely the salts of the weak carbonic acid. Indeed, said M. Roloff,

Die Zusammensetzung des Gemisches ist dabei von den zufälligen Nebenumständen abhängig ; die bestimmte Formel eines basischen Karbonates aufzustellen ist daher von vornherein aussichtslos.

The *magnesia alba* of pharmacy is a basic carbonate of very indefinite composition ; it is obtained by precipitating soln. of the sulphate, chloride, or nitrate with alkali carbonate. A soln. of magnesium sulphate may be employed, also many mineral waters, salt springs, or the mother liquor of sea-water. If these liquids likewise contain calcium salts these must be first removed by adding an alkali sulphate to the liquid. E. Durand, and E. Schmidt have described the preparation of *magnesia alba* in detail. W. Esch made it by the action of ammonia and carbon dioxide on a paste made of water and calcined magnesia. F. Oswald described the preparation from the mineral waters at Bilin ; H. Endemann from the residue remaining after the calcination of magnesite for its carbon dioxide. For the preparation from dolomite, *vide supra*.

The light white powder obtained by mixing soln. of 10 parts of magnesium sulphate and 12 parts of sodium carbonate crystals, each dissolved in 80 parts of water ; boiling for 15 mins. ; washing ; draining ; and drying, is the so-called *light magnesium carbonate*, or the *magnesii carbonas levis* of the pharmacopœia. Under

the microscope it consists of amorphous granules and slender prismatic crystals. In the preceding operations, if 20 instead of 80 parts of water be employed; the mixture evaporated to dryness; the residue washed until all the soluble sulphate is removed; and dried, the resulting white granular powder is the *heavy magnesium carbonate*, or the *magnesii carbonas ponderosus* of the pharmacopœia. Both products are basic carbonates. W. C. Anderson's analyses of commercial samples of heavy carbonate correspond with 41 : 20 : 83, or approximately $MgCO_3.Mg(OH)_2.3H_2O$; of the light carbonate, 39 : 19 : 85, or approximately $MgCO_3.Mg(OH)_2.3\frac{1}{2}H_2O$; and of the so-called crystal carbonate, 24 : 14 : 85, or approximately $3MgCO_3.2Mg(OH)_2.16H_2O$.

The mineral *hydromagnesite*, analyzed by T. Wachtmeister, F. von Kobell, J. L. Smith and G. J. Brush, G. C. Hoffmann, and G. Tschermak, is a basic magnesium carbonate with a composition 4 : 3 : 4, or $3MgCO_3.Mg(OH)_2.3H_2O$—a kind of native *magnesia alba*. J. D. Dana considered the crystals belonged to the monoclinic system, with axial ratios $a : b : c = 1{\cdot}0379 : 1 : 0{\cdot}4652$, and $\beta = 90°$. E. Weinschenk and P. Groth also place the crystals in the monoclinic system, but G. Tschermak and L. Brugnatelli favour the rhombic system. J. L. Smith and G. J. Brush found the sp. gr. of a sample from Texas to be 2·145–2·180; E. Weinschenk found with a sample from Lancaster, 2·32; and L. Brugnatelli found with a sample from Aostatal, 2·196–2·210. The latter also gave the index of refraction $\mu_\beta > 1{\cdot}530$, and $\mu_\gamma > 1{\cdot}538$. The hardness on Mohs' scale is $3\frac{1}{2}$. G. A. Young has reported on the large deposits of hydromagnesite near Atlin, British Columbia, where it occurs as a white soft mineral which falls to powder on drying. The so-called *lancasterite* of B. Silliman is considered by J. L. Smith and G. J. Brush to be a mixture of brucite and hydromagnesite. The amorphous mineral *giorgiosite* found by A. Lacroix at Vesuvius is a 4 : 3 : 3-carbonate, or $3MgCO_3.Mg(OH)_2.2H_2O$. The mineral *hydrogiobertite* found by E. Scacchi near Pollena (Vesuvius) has a composition corresponding with 2 : 1 : 3-carbonate, or $MgCO_3.Mg(OH)_2.2H_2O$. Its sp. gr. is 2·149 to 2·174; L. Brugnatelli's optical study of this mineral inclines him to the opinion that it is a mixture of at least two other minerals. F. Zambonini identified hydrogiobertite with hydromagnesite. L. Brugnatelli found monoclinic prismatic crystals of the Italian mineral *artinite*—named after E. Artini, at Val Brutta, Val Malenco, and Val Lanterna. Analyses correspond with the 2 : 1 : 3-carbonate, or $2MgCO_3.Mg(OH)_2.3H_2O$; its sp. gr. is 2·028 at 21·6°, and 2·013 at 22°; and its hardness is about $2\frac{1}{2}$.

J. J. Berzelius showed that the composition of *magnesia alba* is influenced (i) *by the relative quantity of the precipitant*—if an excess of the alkali carbonate is used, the precipitate is more dense than when the magnesium salt is in excess; (ii) *by the concentration of the solutions*—the more conc. the two soln., the denser the precipitate, and the more normal carbonate does it contain; and (iii) *on the temperature*—the precipitate formed in the cold is lighter than when the soln. are warm, and the utmost degree of lightness is obtained by allowing the precipitate to freeze while still moist. J. J. Berzelius continued: the precipitate formed in the cold approaches more nearly to the composition of the normal salt than that formed in hot soln.; at the same time, a quantity of magnesia remains in soln., because the normal salt is hydrolyzed by water into an insoluble basic salt, and a soluble acid salt. When heated, carbon dioxide is given off by the soln., and the greater part of the magnesia is precipitated from the soln., and the precipitate becomes more basic owing to the escape of carbon dioxide. The composition of the precipitate also depends on (iv) *the time the precipitate is in contact with the mother liquid*. J. J. Berzelius showed that when boiled for a long time, the precipitate has the composition $MgO : CO_2 : H_2O = 4 : 3 : 4$. According to J. Fritzsche, if moderately boiled, the precipitate is converted into the 5 : 4 : 4-carbonate, but if long boiled, it becomes mixed with a constantly increasing proportion of the 4 : 3 : 4 and the 3 : 2 : 3-carbonates. In general, it may be said that *every alteration in the conditions of preparation of magnesia alba tends to modify the composition of the product*. W. A. Davis found traces of alkali in the soln. caused "a wide variation in the results."

Analyses of *magnesia alba* have been made by J. Fritzsche, J. J. Berzelius, H. Rose, O. Brill, K. Kraut, H. Beckurts, E. A. Nörgaard, W. C. Anderson, etc., and many of the results have been represented by chemical formulæ and assumed to be definite compounds without the application of any criterion as to whether

mixtures or individuals are in question. J. J. Berzelius favoured the formula 4 : 3 : 4 ; but J. Fritzsche and R. Rinne showed that while the original precipitate approaches 5 : 4 : 5 in composition, this by the prolonged action of boiling water approaches 4 : 3 : 4, and afterwards 3 : 2 : 3. G. Rose observed that the product obtained by evaporating the acid carbonate on a water-bath includes spherules of magnesia alba with crystals of the normal salt resembling aragonite. E. A. Nörgaard failed to obtain a definite crystalline basic carbonate. L. Joulin argued that *magnesia alba* is a mixture of magnesium hydroxide and carbonate in proportions dependent on the conc., temp., and the relative proportions of the reacting salts. As previously indicated, W. A. Davis has shown that trihydrated magnesium carbonate, $MgCO_3.3H_2O$, may be regarded as **dihydrated magnesium hydroxyhydrocarbonate,** $Mg(HCO_3)OH.2H_2O$, which is produced by the hydrolysis of a soln. of magnesium hydrocarbonate. The dihydrate is readily converted into anhydrous **magnesium hydroxyhydrocarbonate,** $Mg(HCO_3)OH$, as indicated in connection with trihydrated magnesium carbonate, where the preparation and properties of the hydroxycarbonates are therefore discussed. When the dihydrated hydroxycarbonate is suspended in boiling water, it slowly decomposes into magnesium hydroxide. The solid at any intermediate stage has a composition ranging between $Mg(HCO_3)OH.2H_2O$ and $Mg(OH)_2$, and the mixed character of the product is evident from a microscopic examination of the mass. Excluding the hydroxycarbonate and its hydrate, W. A. Davis shows good reasons for believing that all the varieties of basic magnesium carbonate, magnesia alba, light, heavy, and crystal magnesium carbonates are not definite salts, but mixtures of the anhydrous and dihydrated magnesium hydroxycarbonates and hydroxide in varying proportions.

Hydromagnesite, and magnesia alba, decompose at a lower temp. than magnesite (*q.v.*) ; the latter decomposes into magnesium oxide and carbon dioxide at 300°. According to P. Kremers, a litre of water at 15° dissolves 0·197 part of magnesia alba ; and, according to A. Bineau, 0·10 part in cold or boiling water. According to A. M. Pleischl, the aq. soln. has an alkaline reaction. S. Merkel found that with a soln. of carbon dioxide in a litre of water and at different press. :

Press. of CO_2	1	2	4	5	6 atm.
MgO dissolved	1·314	1·344	7·46	9·09	13·1 grms.

so that the solubility increases with increasing press. of carbon dioxide when the temp. is constant. G. C. Wittstein found the solubility in water is much raised in the presence of ammonium nitrate, and, according to A. Vogel, in the presence of ammonium chloride. Magnesia alba does not dissolve so quickly after it has been heated to 100° ; according to A. Vogel, the sat. soln. does not become turbid on exposure to air or by boiling ; but it is precipitated by potassium hydroxide. Magnesia alba is readily soluble in acids. According to T. S. Hunt, magnesia alba precipitates calcium carbonate from its soln. in carbonated waters ; and G. Bauck found that when magnesia alba is boiled with a dil. soln. of calcium chloride the precipitate contains $CaCO_3 : Mg(OH)_2$ in the mol. proportion 3 : 1. According to C. A. Gössmann, if carbon dioxide be passed into a soln. of sodium chloride containing calcium sulphate and magnesia alba, magnesium chloride, sodium sulphate, and calcium carbonate are formed. E. Fleischer digested eq. quantities of *magnesia alba*, calcium sulphate, and a soln. of sodium chloride (1 : 6) for an hour at 80°, and found 30 per cent. of the calcium sulphate was transformed into carbonate ; the change is less complete if the salt soln. be more dil., if some magnesium sulphate be present, and if the mixture be kept cold.

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§ 18. Complex or Double Salts with Magnesium Carbonate

According to J. J. Berzelius,[1] an aq. soln. of magnesium nitrate or chloride, when mixed with an excess of sodium hydrocarbonate, furnishes crystals similar to those obtained when potassium hydrocarbonate is used as precipitant, and presumably misled by analogy, he assumed the crystals to be *sodium magnesium hydrocarbonate*, $MgCO_3.NaHCO_3.4H_2O$. He added that the crystals are not so readily decomposed by water as the *potassium magnesium hydrocarbonate*, $MgCO_3.KHCO_3.4H_2O$. H. St. C. Deville, J. Fritzsche, H. Rose, E. A. Nörgaard, and G. von Knorre did not succeed in verifying Berzelius' assumed sodium salt ; nor did they obtain the tetrahydrate, $Na_2CO_3.MgCO_3.4H_2O$. G. Mosander treated a warm soln. of a magnesium salt with an excess of sodium carbonate, and obtained a granular precipitate containing about 21 per cent. of sodium carbonate, and 79 per cent. of magnesium carbonate. The solid dissolved in water as a whole without separating the sodium salt, but, added J. J. Berzelius, if the compound be decomposed by ignition, the sodium salt may be leached out. The alkali magnesium carbonates are decomposed by water. K. Kippenberger mixed freshly precipitated magnesium carbonate with a soln. of sodium or potassium hydrocarbonate at ordinary temp., and found much magnesium carbonate dissolves, and crystallizes from the filtered soln. in about 24 hrs. The crystals approximate $MgCO_3.3H_2O$. It is assumed that an alkali magnesium double carbonate is formed and afterwards decomposed.

G. Bollmann prepared what were regarded as hexagonal plates of **lithium magnesium tricarbonate,** $2Li_2CO_3.MgCO_3$, by dropping 4·6 c.c. of a 10 per cent. soln. of magnesium chloride into 100 c.c. of a sat. soln. of lithium carbonate. After the mixture has stood 4–6 weeks, the turbid soln. is clear, the hydrated magnesium carbonate has disappeared, and six-sided plates of this double salt appear. The crystals are but slowly decomposed by water. The crystals are hard enough to scratch glass.

H. St. C. Deville digested magnesia alba with an aq. soln. of sodium hydrocarbonate at 60°–70°, and obtained anhydrous **sodium magnesium carbonate,** $Na_2Mg(CO_3)_2$; G. von Knorre obtained the same salt by digesting trihydrated magnesium carbonate with an aq. soln. of sodium sesquicarbonate for 24 hrs. between 63°–65°, filtering the warm mixture, and washing well the solid. A. de

Schulten prepared the same compound by heating on a water-bath for 4–5 hrs. a mixture of soln. of 100 grms. of anhydrous sodium carbonate in 400 grms. of water, and 20 grms. of magnesium nitrate in 50 grms. of water, rhombohedral or tetragonal crystals are formed which, he said, were uniaxial, and had a sp. gr. of 2·729 at 15°—G. von Knorre stated that his crystals were doubly refracting, and probably belonged to the tetragonal system. Both A. de Schulten and G. von Knorre agreed that the double salt is very slowly decomposed by cold water; and even at 100° the speed of decomposition is not fast. According to H. St. C. Deville, carbon dioxide and traces of water are lost when the crystals are ignited and the double salt is therefore assumed to be anhydrous. E. A. Nörgaard obtained the **pentadecahydrated sodium magnesium carbonate,** $Na_2CO_3.MgCO_3.15H_2O$, in rhombic prismatic crystals, by cooling to a low temp. a soln. of magnesium sulphate made just turbid with sodium carbonate. The crystals are decomposed by water, and should be washed with the clear mother liquid and then pressed. Magnesia alba is formed when the crystals are boiled with water. Attempts made by H. St. C. Deville, E. A. Nörgaard, J. Fritzsche, H. Rose, V. A. Jacquelain, G. Kittel, K. Kippenberger, G. von Knorre, and G. Bollmann furnished a basic magnesium carbonate.

Crystals corresponding with **sodium magnesium chlorocarbonate,** $NaCl.Na_2CO_3.MgCO_3$, were found by G. W. Leighton on the inside of an iron boiler in which the vapour of ammonium carbonate was passed through a lye containing sodium and magnesium chlorides; C. Winkler found them on the inside of the cooling apparatus of the Solvay soda process; and J. H. Pratt found them native at Borax Lake, San Bernadino County, Cal., and called the mineral *northupite*. A. de Schulten obtained the salt by heating a mixture of soln. of 15 grms. of magnesium chloride in 50 c.c. of water, and of 20 grms. anhydrous sodium carbonate and 150 of sodium chloride in 500 c.c. of water. The flocculent precipitate gradually forms regular octahedral crystals which are washed with the mother liquid, and dried at 100°. The crystals belong to the cubic system. C. Winkler represented the salt by the formula $Na_3(MgCl)(CO_3)_2$, and S. L. Penfield and G. L. Jamieson, by

$$\begin{matrix} NaO \\ Cl.Mg.O \end{matrix}\!\!>\!C\!<\!\begin{matrix} O\text{—}C(ONa)_2\text{—}O \\ O\text{—}C(ONa)_2\text{—}O \end{matrix}\!\!>\!C\!<\!\begin{matrix} ONa \\ O.Mg.Cl \end{matrix}$$

A. de Schulten gives 2·377 for the sp. gr. of the artificial crystals at 15°; and J. H. Pratt, 2·380 for northupite. The hardness of the mineral is 4. The crystals melt at a red heat, forming an enamel-like mass from which water extracts sodium carbonate and chloride, leaving magnesium oxide as a residue. J. H. Pratt gives 1·5117 for the index of refraction in Li-light; 1·5144 in Na-light; and 1·5180 in Tl-light. The crystals are stable in air, but slowly decomposed by cold or hot water.

The sodium and potassium magnesium carbonates are fundamentally different, so that H. St. C. Deville was led to say:

> Dans aucun cas la soude et la potasse, dont les analogies sont si intimes, ne se séparent d'une manière plus complète que lorsqu'elles sont mises dans les conditions nécessaires pour former les mêmes carbonates double métalliques.

The double carbonates with rubidium, cæsium, and thallium show more analogies. P. A. von Bonsdorff, and H. Rose treated a warm soln. of a magnesium salt with an excess of potassium carbonate, and obtained a precipitate which is slightly soluble in water, and separates from its soln. as a crystalline powder. If the soln. are mixed at the b.p., magnesium carbonate is alone precipitated. J. J. Berzelius prepared crystals of what were probably **tetrahydrated potassium magnesium carbonate,** $K_2Mg(CO_3)_2.4H_2O$, by treating a cold aq. soln. of magnesium nitrate or chloride with an excess of potassium sesquicarbonate, and allowing the mixture to stand for a few days. H. St. C. Deville made small rhombic prisms of the same salt by digesting magnesia alba with an aq. soln. of potassium hydrocarbonate for 12 to

15 hrs. at 60° to 70° ; G. von Knorre prepared crystals of the salt by digesting 9 grms. of trihydrated magnesium carbonate and 50 grms. of potassium hydrocarbonate, with 50 c.c. of water for 21 hrs. at 60° to 70°, and by digesting 20 grms. of hexahydrated magnesium chloride and 40 grms. of potassium carbonate for two days at ordinary temp. If magnesium sulphate be used the precipitate is contaminated with sulphates. H. St. C. Deville found that the crystals are decomposed by cold water ; and he gives for the axial ratios of the rhombic crystals $a : b : c = 0{\cdot}7563 : 1 : 0{\cdot}6068$.

J. J. Berzelius found that if an excess of potassium hydrocarbonate be added to a cold aq. soln. of magnesium chloride or nitrate, large crystals of **tetrahydrated potassium magnesium hydrocarbonate,** $KHMg(CO_3)_2.4H_2O$, or $Mg(KCO_3)(HCO_3).4H_2O$, are formed. In his study of the solubility of magnesium carbonate in soln. of potassium hydrocarbonate, F. Auerbach obtained the same salt. G. von Knorre made this salt by adding a very conc. soln. of 6 grms. of magnesium chloride to 50 c.c. of a soln. with 10 grms. of potassium hydrocarbonate, and 7 grms. of the normal carbonate—crystals are formed when the mixture is allowed to stand. R. Engel obtained this salt by the action of carbon dioxide on a soln. of potassium chloride and trihydrated magnesium carbonate ; and the Salzbergwerk Neu-Stassfurt has some patents on the subject.

In *R. Engel's magnesia-potash process*, magnesium carbonate, $MgCO_3.3H_2O$, is suspended in a sat. soln. of potassium chloride, and the mixture sat. with carbon dioxide. A crystalline double salt, $MgCO_3.KHCO_3.4H_2O$, separates from the soln. : $3(MgCO_3.3H_2O)+2KCl+CO_2 = MgCl_2+2(KHCO_3.MgCO_3.4H_2O)$. When the crystalline mass is treated with water at 140° under press., carbon dioxide is evolved, magnesium hydroxide is precipitated, and potassium carbonate remains in soln. : $2(KHCO_3.MgCO_3.4H_2O)=K_2CO_3+2Mg(OH)_2+7H_2O+3CO_2$. Sodium carbonate cannot be formed in the same way since the corresponding sodium salt, $MgCO_3.NaHCO_3.4H_2O$, does not precipitate.

According to J. C. G. de Marignac, the crystals belong to the triclinic system and have the axial ratios $a : b : c = 0{\cdot}4261 : 1 : 0{\cdot}5945$, and the axial angles $\alpha = 111° 9'$, $\beta = 114° 26'$, and $\gamma = 74° 33'$. G. von Knorre gives for the sp. gr. 1·984 at 18°. J. C. G. de Marignac found the crystals to be stable in air. J. J. Berzelius added that the crystals are tasteless at first, but after a few seconds exhibit an alkaline flavour. When heated to 100° the crystals become opaque and lose water ; and when strongly heated they soften and give off bubbles of carbon dioxide leaving a mixture of magnesium oxide and normal potassium carbonate. The crystals are soluble in water, but not without decomposition, for a basic magnesium carbonate is precipitated and a mixture of potassium hydrocarbonate and magnesium hydrocarbonate passes into soln. J. Fritzsche said that the precipitate is trihydrated magnesium carbonate mixed with the pentahydrate, and the proportion of the latter increases as the temp. of the water falls. G. von Knorre said that the salt is stable in water sat. with carbon dioxide.

R. Engel has investigated the conditions under which normal magnesium carbonate combines with potassium hydrocarbonate, and finds that for the same soln. of potassium hydrocarbonate the velocity of the reaction decreases as the temp. rises. If the temp. remains constant, the velocity increases with the initial conc. of the potassium soln. Combination ceases when it attains a certain limit, which is measured by the conc. of the soln. of the potassium salt remaining in contact with excess of magnesium carbonate without combining with it. This limit increases with the temp., and its variation is given by the formula $y = 2{\cdot}5236 + 0{\cdot}00517t + 0{\cdot}003108t^2$, where y is the number of c.c. of standard sulphuric acid required to neutralize the carbonates remaining in soln. The product of the combination, $MgCO_3.KHCO_3+4H_2O$, is decomposed by water, and the decomposition tends towards a limit which is not identical with the limit of combination, but is always inferior to it by a quantity which is practically the same for all temp. P. Duhem regards this as an example where *la région des faux équilibres* separates two regions corresponding respectively to two reactions which are the inverse of one another.

The reaction was also investigated by E. H. Büchner, and he considers that R. Engel's systems were not in equilibrium, nor could M. Nanty confirm the existence of two distinct limits in the formation and decomposition of the system: $KHCO_3 + MgCO_3.3H_2O + H_2O \rightleftharpoons MgCO_3.KHCO_3.4H_2O$, at 20°–30°; since he found at the same temp. and press., the two reactions converge towards a common limit. F. Auerbach studied the conditions of stability as indicated in connection with the solubility of magnesium carbonate in soln. of potassium hydrocarbonate.

H. Erdmann and P. Köthner prepared **tetrahydrated rubidium magnesium hydrocarbonate,** $MgRbH(CO_3)_2.4H_2O$, by heating on a water-bath at 60° in a current of carbon dioxide, a soln. of rubidium hydrocarbonate, and magnesium carbonate. The salt is very efflorescent. G. Bollmann prepared the same salt, and he also obtained microscopic rhombic plates of tetrahydrated **rubidium magnesium carbonate,** $MgCO_3.Rb_2CO_3.4H_2O$, mixed with trihydrated magnesium carbonate, $MgCO_3.3H_2O$, by adding rubidium carbonate to a well-cooled soln. of magnesium chloride. He likewise obtained tetrahydrated **cæsium magnesium carbonate,** $MgCO_3.Cs_2CO_3.4H_2O$. Both salts are readily decomposed by water. G. Bollmann also speaks of a possible *copper magnesium carbonate.*

According to A. F. de Fourcroy,[2] the addition of even a large excess of aq. ammonia to a soln. of a magnesium salt never precipitates more than half the magnesia present; and, according to N. J. B. G. Guibourt, one part of ammonium sesquicarbonate precipitates half the magnesium as carbonate from a soln. of two parts of magnesium sulphate; and two parts of ammonium sesquicarbonate precipitate all the magnesium as tetrahydrated **ammonium magnesium carbonate,** $(NH_4)_2CO_3.MgCO_3.4H_2O$. F. Schaffgotsch said the precipitate is at first flocculent, but later becomes crystalline. When a mixture of cold aq. soln. of magnesium sulphate or chloride and ammonium sesquichloride is allowed to stand for several hours, A. F. de Fourcroy and C. F. Bucholz observed that crystals of the double salt are formed. G. C. Wittstein also found a soln. of magnesia in an aq. soln. of ammonium sesquicarbonate furnishes a crop of crystals of the double salt in a short time. P. A. Favre observed similar results on shaking magnesia alba with an aq. soln. of ammonium carbonate, and allowing the filtered soln. to crystallize. According to F. Schaffgotsch, soln. of ammonium carbonate, with or without free ammonia, furnish the double salt on being treated with a magnesium compound; and E. Divers added that if a soln. with one mol of magnesium sulphate be treated with less than four mols of ammonium carbonate, magnesium carbonate first precipitates, and the double salt is afterwards deposited: if the soln. contains two mols of ammonium chloride for every mol of magnesium sulphate, no magnesium carbonate is precipitated. If the ammonium carbonate is added slowly, the double salt is formed, and all the magnesium is precipitated as the double salt when four mols of ammonium carbonate have been added; if a larger proportion of ammonium chloride is present, more ammonium carbonate is required for the complete precipitation of the magnesium. R. Weber and F. Schaffgotsch studied the occlusion of salts by the precipitated ammonium magnesium carbonate; they find potassium salts are occluded so tenaciously as not to be removed by washing—sodium salts are not so occluded. According to J. W. Döbereiner, the crystals form translucent rhombohedrons. N. J. B. G. Guibourt observed that the damp crystals give off ammonia when exposed to air, but not if the crystals have been well dried over calcium chloride. E. Divers found that the dry distillation of the double salt gives a liquid which deposits crystals of ammonium sesquicarbonate, $(NH_4)_4H_2(CO_3)_3.H_2O$, and a sublimate of the same salt. The ignition of the salt yields magnesium oxide. According to C. F. Bucholz, the crystals are decomposed by water; and P. A. Favre, N. J. B. G. Guibourt, and E. Divers found that with cold water, magnesium carbonate is formed, and with hot water, magnesia alba. According to E. Divers, the double salt is sparingly soluble in an aq. soln. of ammonium carbonate, and very soluble in an aq. soln. of ammonium chloride. If a magnesium salt be treated with a large excess of ammonium hydrocarbonate, H. St. C. Deville obtained

tetrahydrated **magnesium ammonium hydrocarbonate,** $Mg(NH_4CO_3)(HCO_3).4H_2O$, as a crystalline powder which forms normal ammonium magnesium carbonate by the loss of ammonia and water. A higher hydrate, $Mg(NH_4CO_3)(HCO_3).5\frac{1}{2}H_2O$, is produced by working at a low temp. R. Engel could not make this salt, but G. von Knorre succeeded in doing so.

The term *dolomite* is employed somewhat loosely for limestones containing notable quantities of magnesium carbonate; and it is also employed in a more specific sense for the double **calcium magnesium carbonate,** $CaMg(CO_3)_2$, which occurs as a crystallized mineral and as a massive rock, and in which the ratio CaO : MgO is as 1 : 1. H. B. Saussure[3] first named the mineral *dolomie* after D. Dolomieu, who observed many of the peculiar properties of what he called *pierres calcaires très-peu effervescentes avec les acides;* R. Kirwan called it *dolomite.* Normal dolomite has also been called *dolomite spar*, *bitter spar*, or *bitter salt spar.* In some cases part of the magnesium has been replaced by iron to furnish *ferruginous dolomites*, which, when coloured brown, are called *brown spar*, and, when coloured a pale brown, *pearl spar;* while varieties approximating to $2CaCO_3.MgCO_3.FeCO_3$ are called *ankerite*, after M. Anker of Styria. Varieties of dolomite of minor importance have been named after particular localities—*e.g. miemite* from Miemo (Tuscany), *tharandite* from Tharand (Dresden), and *gurhofite* from Gurhof (Austria). The latter was analyzed by A. Baumgarten and J. R. von Holger in 1837, and was shown by H. von Foullon to be most probably a mixture. L. Blum found what he regarded as $2MgCO_3.CaCO_3$ in an iron mine in Lothringen, and he regarded it as a new mineral species, *lessbergite;* but W. Bruhns showed that lessbergite is probably a mixture. Several more or less ephemeral names have been used for varieties of dolomite—*conite, brossite, tautocline*, etc. What appears to have been a kind of ankerite was analyzed by P. Woulfe in 1779. Similarly also manganese carbonate may replace magnesium carbonate, furnishing *manganiferous dolomites*—a specimen from Kuttenberg (Bohemia) was named *kutnohorite* by A. Bukowsky. A *nickeliferous dolomite* from Taraps (Switzerland) has been called *taraspite* by C. von John; a *cobaltiferous dolomite* was reported by W. Gibbs from Przibram; and a zinciferous dolomite by K. Monheim from Altenberg. There are also *dolomitic marbles.* The magnesian limestones are presumably mixtures of dolomite and calcite, although brucite is sometimes present—*e.g. predazzite* and *pencatite* are mixtures of calcite and brucite.

Dolomite, like limestone, is found in large beds covering whole tracts of country and mountain ranges, as in the North of England, Tyrol, and many other places. Numerous analyses have been made of normal dolomites and dolomites with a low proportion of iron;[4] of ferruginous dolomites, including ankerite and brown spar;[5] and of manganiferous dolomites.[6]

The formation of dolomite in nature.—In the formation of marine dolomites in nature, (i) the mixed carbonates may be directly precipitated in shallow waters, by changes of temp., of conc. of atm. carbon dioxide, or by ammonium carbonate derived from the decomposition of marine organisms. This hypothesis has been advocated by G. Leube,[7] C. W. Gümbel, T. Scheerer, T. S. Hunt, etc. (ii) The limestone formed by the accumulation of the shells or skeletons of marine organisms is magnesian. This statement is emphasized by A. G. Högbom's analyses of oceanic oozes; and by F. W. Clarke and W. C. Wheeler's analyses of the inorganic parts of marine organisms, etc. The more soluble calcium carbonate may be leached away by percolating waters until the dolomitic ratio is approximated. H. Grandjean, A. G. Högbom, J. D. Dana, and others have produced evidence of this action. The borings on the atoll of Funafuti, examined by J. W. Judd, showed a marked enrichment in magnesium carbonate near the surface, owing presumably to the leaching out of the lime salts. The coralline rock may also be enriched by the magnesium salts contained in sea-water. The precipitation of magnesium carbonate from its soln. in sea-water by calcium carbonate has been established by the experiments of T. Scheerer and F. Hoppe-Seyler. T. Scheerer noted that powdered chalk

precipitates magnesium carbonate from a soln. of the hydrocarbonate, and carbonated waters can dissolve calcium carbonate out of magnesian limestones.

The synthesis of dolomite.—J. C. G. de Marignac obtained dolomite artificially by heating calcium carbonate with a soln. of magnesium chloride to 200° under 15 atm. press. After 2 hrs.' heating a little of the calcium carbonate was dolomitized, but after 6 hrs.' heating, the product was richer in magnesite than is dolomite itself. A. von Morlot heated powdered calcite with a soln. of magnesium sulphate in a sealed tube at 200° and found that a mixture of dolomite and gypsum was formed; W. Haidinger pointed out that these two minerals are in frequent association. This reaction appears to be reversible because H. C. Sorby obtained efflorescences of magnesium sulphate in Permian limestones, and they are not uncommon in gypsum quarries. J. Durocher heated fragments of porous limestone with dry magnesium chloride to dull redness in a closed gun-barrel so that the vapour of the chloride impregnated the carbonate. The limestone was partially changed to dolomite. H. St. C. Deville saturated chalk or corals with a soln. of magnesium chloride, and heated the mixture on a sand-bath. The lime was partially replaced by the magnesia. K. Spangenberg heated vaterite with a soln. of sodium carbonate and magnesium chloride at 180°–200° in an autoclave under a press. of 50 atm. of carbon dioxide, and obtained dolomite. G. Linck effected the synthesis of dolomite by adding calcium chloride to a mixture of soln. of magnesium chloride, magnesium sulphate, and ammonium sesquicarbonate, when the amorphous precipitate becomes crystalline, with the composition and optical properties of dolomite, when gently heated in a scaled tube. W. Meigen failed to verify G. Linck's result. L. Bourgeois and H. Traube obtained dolomite by heating a mixture of magnesium and calcium chlorides with potassium cyanate in a sealed tube at 130°. F. W. Pfaff found that the products of organic decay—ammonium carbonate and sulphide, hydrogen sulphide, etc.—probably assist in the dolomitic process; he found that when a current of carbon dioxide is passed for a long time through a warm soln. of the sulphates and chlorides of magnesium and calcium, the slow evaporation of the soln. at 20°–25°, yields a residue containing a double carbonate insoluble in dil. hydrochloric acid. It is suggested that these conditions might be approximately paralleled in the case of sea-water and thus dolomite might be formed.

C. J. B. Karsten found magnesium carbonate dissolves slowly in a conc. soln. of calcium chloride, and the freshly precipitated carbonate was found by T. S. Hunt to dissolve copiously in that menstruum. According to C. A. Gössmann, the soln. decomposes when boiled, forming a precipitate of calcium carbonate and magnesium chloride. The spontaneous evaporation of a soln. of calcium and magnesium carbonates in carbonated water mixed with calcium chloride was found by A. Bineau to give a precipitate of calcium carbonate, and if evaporated by the aid of heat, a precipitate of calcium carbonate mixed with a little magnesium carbonate. G. Bauck boiled a soln. of equal parts of magnesium and calcium carbonates in carbonated water along with some calcium and magnesium chlorides, and found the precipitate contained a larger proportion of calcium than magnesium the more prolonged the boiling. With slow heating very little, and with rapid heating a lot, of magnesium salt is precipitated; when the alkaline liquid is allowed to stand some days, the magnesium precipitate is redissolved. According to T. S. Hunt, sodium hydrocarbonate precipitates at first almost wholly calcium carbonate from a mixed soln. of calcium and magnesium chlorides; and then follows hydrated magnesium carbonate. T. S. Hunt precipitated mixtures of calcium and magnesium carbonates from hydrocarbonate soln. by alkali carbonates; when the pasty mass formed by precipitation was heated to a temp. exceeding 120°, combination occurred, and dolomite was formed. T. Scheerer obtained mixtures but no dolomite when a soln. of calcium and magnesium hydrocarbonates is evaporated spontaneously at ordinary temp. Temp. is evidently an important factor in the formation of dolomite. F. Hoppe-Seyler obtained no dolomite by allowing a soln. of magnesium chloride to act on calcium carbonate for many months; nor by allowing sea-water,

sat. with carbon dioxide, to stand in contact with an excess of calcium carbonate, for four months in a closed flask; but when magnesium salts or sea-water were heated with calcium carbonate in sealed tubes, dolomite and magnesite were formed. Calcium carbonate heated to over 100° with a soln. of magnesium hydrocarbonate gave a similar result.

C. Klement tried aragonite, the less stable form of calcium carbonate, in place of calcite, and he found that a conc. soln. of magnesium sulphate at 60° will partially transform coral or aragonite into magnesium carbonate under conditions where calcite is but slightly attacked; a mixed soln. of magnesium sulphate and sodium chloride at 90° attacked aragonite rapidly, forming a product with 41·5 per cent. of magnesium carbonate. Magnesium chloride was not so active as the sulphate. Although the product of these reactions is not dolomite, but rather a mixture of the carbonates, he believed that in time mixtures of this kind would combine and crystallize into dolomite. He attributed the formation of dolomite to the action of sea-water in closed lagoons on the aragonite of coral rock. Pseudomorphs of dolomite after calcite have been reported by R. Blum, and others.

The deposition of crystalline dolomite, and of magnesian travertine, from natural waters has been observed, as well as, what might be called, the accidental formation of dolomite crystals. Thus, J. Girardin noted that the travertine deposited by the mineral spring of St. Allyre (Clermont) is rich in magnesium carbonate, but whether present as dolomite has not been ascertained. A. Moitessier found that crystals of dolomite were deposited inside a badly closed bottle containing mineral water; and A. Terreil found similar crystals were formed in a sealed tube containing water from a hot spring near the Dead Sea. Hence, L. Lartet concluded that the dolomites in the region of the Dead Sea were probably formed by the impregnation of limestones by magnesian waters. E. von Gorup-Besanez also found spring water from the dolomites of the Jura, containing calcium and magnesium carbonates in the dolomitic (1 : 1) ratio, to deposit the mixed salts and not the double compound. Although in the laboratory, a moderately high temp. is needed for the combination of the mixed carbonates to form the double salt, it may be that union between the moist particles does actually take place very slowly in the cold and possibly under a moderate press.

The properties of dolomite.—The **crystals** of dolomite are shown by P. Groth [8] to belong to the trigonal system and to have the axial ratio $a : c = 1 : 0{\cdot}8322$, and $\alpha = 102° 53'$. H. Baumhauer, P. Koller, etc., have studied the **corrosion figures.** G. Tschermak has pointed out that the corrosion figures show that dolomite is not hemihedral like calcite, but rather tetartohedral; and this is in agreement with F. Becke's observations on the twinning of dolomite crystals. In order to explain the magnesia in calcites, P. Groth assumed an isomorphism between calcite and dolomite, and he regarded the latter as a true double salt; but F. Becke, *au contraire*, showed that while the crystals of calcite and magnesite belong to the scalenohedral class, dolomite crystallizes in the rhombohedral class. The **X-radiograms** of dolomite have been studied by H. Haga and F. M. Jäger, F. Rinne, and A. Johnsen.

The **specific gravity** of dolomite has been determined on most of the samples which have been analyzed—*vide supra*—and the results range from 2·75 to 3·10. Most of these samples were not of a high degree of purity. F. E. Neumann's value [9] is 2·916; F. Ott's, 2·89; G. Tschermak's, 2·924; E. Madelung and R. Fuchs' 2·8735 (0°); and F. Senft's 2·85. The best representative value for dolomite is taken by J. W. Retgers to be 2·872; for calcite, 2·712; and for magnesite, 3·017. The mean sp. gr. calculated on the assumption that dolomite is a mechanical mixture is 2·843, a difference of 0·029. The contraction which occurs in the formation of dolomite is therefore taken by J. W. Retgers to indicate that dolomite is a chemical individual, a true double salt. This double salt does not form isomorphous mixtures with either calcite or magnesite, but stands isolated in its physical properties outside the series of mixtures. The primitive forms of calcite and magnesite are two rhombohedra with slightly different angles; and these angles vary with the temp.

and elastic actions. Calcium carbonate, however, can form a very small range of mixed crystals with a little magnesium carbonate, and these crystals are isomorphous with those of calcite, so that the magnesite here occurs as a labile dimorphous modification which does not belong to the same class as calcite. Similarly also with respect to the admixture of a little calcite with magnesite, the calcite is present as a labile modification isomorphous with magnesite. To summarize, it is probable, though not yet established, that dolomite is a double salt; but there is yet no further evidence of the assumed isodimorphism of calcite and magnesite, *viâ* two unknown labile phases. The **hardness** of dolomite on Mohs' scale is 3·5 to 4·0. W. Voigt found the **elastic modulus** to be 14,600 kgrms. per sq. mm. in the direction of the principal axis; 8330 kgrms. per sq. mm. in a direction perpendicular to that axis; 14,400 and 18,700 kgrms. per sq. mm. respectively in directions inclined at angles −21·5° and +21·5° to the principal axis. E. Madelung and R. Fuchs gave $1{\cdot}21\times10^{-6}$ megabars per sq. cm. for the **compressibility** of dolomite.

According to F. Findeisen[10] when dolomite is heated, the magnesium carbonate first decomposes, and then the calcium carbonate. G. A. Bole and J. B. Shaw obtained similar results. K. Friedrich and L. G. Smith found that different specimens of dolomite began to decompose at from 730° to 745°, and the heating curves showed a maximum thermal change at about 750° or 760°. According to J. A. Hedvall and J. Heuberger, if the oxides of the alkaline earths and magnesium be arranged in order of increasing basicity, MgP, CaO, SrO, BaO, then the oxide of the more basic metal will on heating with the carbonate of the less basic element be changed into the carbonate without the evolution of gas and at a temp. well below the temp. of dissociation of the carbonate taken. The temp. of the reaction decreases and the heat effect increases with increasing difference of basicity, for example, $MgCO_3+BaO=BaCO_3+MgO+19$ cals. at 230°; $SrCO_3+BaO=BaCO_3+SrO+6{\cdot}14$ cals. at 280°. According to H. St. C. Deville, and A. Hauenschild, dolomite which has been heated to 360°–400° and made into a paste with water, hardens under water like a cement; but if pre-heated to redness, it disintegrates when placed in water.

The thermal properties of dolomite have not been closely examined, but the same remark applies to the physical properties generally. It is remarkable, said H. Leitmeier, that so little is known about the physical properties of a substance on which so much work, relating to its genesis and constitution, has been expended. H. Fizeau measured the **coefficient of linear expansion,** and found $\alpha=0{\cdot}00001968$ in a direction parallel to the chief axis, and 0·00000367 when vertical to the chief axis. H. Kopp found the coeff. of cubical expansion to be 0·000035 per degree between 13° and 43°. H. Kopp found the **specific heat** to be 0·206 between 18° and 47°; H. V. Regnault, 0·21743 between 26° and 99°; and R. Ulrich and E. Wollny, 0·2218 between 18° and 98°.

According to H. Fizeau, the **double refraction** is strongly negative $\omega-\epsilon=0{\cdot}189$; and the **index of refraction** for Na-light is $\omega=1{\cdot}68174$ for the ordinary ray, and $\epsilon=1{\cdot}50256$ for the extraordinary ray. K. Eisenhut[11] measured the refractive indices of eight specimens of dolomite with gradually increasing proportions of iron, and found that the index of refraction increases. W. Schmidt found the **dielectric constant** of a crystal of dolomite in a direction parallel to the chief axis to be 6·70, and normal to that axis 7·77. W. Voigt studied the **magnetic properties** of crystals of dolomite.

The solubility of dolomite.—According to A. Cossa,[12] a litre of distilled *water* sat. at 18° and 750 mm. press. with carbon dioxide, dissolves 0·320 grm. of dolomite, 0·15 grm. of magnesite, and 1·0 to 1·2 grms. of calcite. H. Leitmeier found that at ordinary temp. a litre of water sat. with carbon dioxide dissolves 0·11 grm. of dolomite. C. G. C. Bischof found that if the dolomite contains a little magnesite or calcite, these are first dissolved. T. Scheerer found that the calcium carbonate was dissolved much faster than magnesium carbonate. C. Doelter and R. Hoernes, and E. von Gorup-Besanez did not find much difference, though the calcium

carbonate dissolved a little more quickly. When the soln. is evaporated, the dissolved carbonates do not reform dolomite, although F. Hoppe-Seyler showed that at temp. near 200°, dolomite can be recrystallized from carbonated water.

The early reports on the action of acids on dolomite and magnesian limestones appear contradictory; possibly some cases can be explained by the presence of forms of magnesium carbonate which dissolve, in acids—some slowly, some quickly. In 1791, D. Dolomieu stated that cold dil. *mineral acids* do not act very well on dolomite. C. J. B. Karsten treated a magnesian limestone with cold dil. acetic acid and obtained an undissolved residue of dolomite; in another limestone, he obtained a residue of magnesium carbonate *ohne Spur von Kalk;* and therefore inferred that the former was a mixture of calcite and dolomite, the latter a mixture of calcite and magnesite. A. Damour similarly treated a limestone from Mt. Somma and found that it all dissolved even though the proportions of calcium and magnesium carbonates were as 4 : 1. C. Schmidt also obtained a similar result with a Russian limestone. P. Forchhammer found that dil. *acetic acid* removed the excess of calcite from a dolomitic limestone, but scarcely affected the dolomite. C. Doelter and R. Hoernes, A. Vesterberg, and F. Hoppe-Seyler obtained a similar result. On the other hand, F. W. Pfaff, J. Roth, and T. S. Hunt found a considerable proportion of magnesium salt was dissolved. K. Haushofer made an extensive study of the solubility of dolomite in acetic acid, and found that the duration of the treatment, the conc. of the acid, and the temp. are of great importance. The effect of temp. and the time of treatment are usually greater with dil. than with conc. acetic acid. With normal dolomites, the magnesia dissolves more readily than the lime, while with dolomites containing an excess of calcite, the calcium salt dissolves faster than the magnesium salt. Citric acid acts more energetically than acetic acid. T. Liebe found that a dolomitic limestone was enriched by treatment with cold dil. *hydrochloric acid* owing to the preferential dissolution of the calcium carbonate, and C. E. Schafhäutl made a similar observation with *nicht allzu* conc. hydrochloric acid. For the action of *carbonic acid*, that is, carbonated water, or a soln. of carbon dioxide in water, see the decalcification of dolomite. A. Vesterberg found that magnesium carbonate in some cases dissolves as fast as the calcium carbonate; and that the presence of magnesium chloride depresses the speed of dissolution of magnesium carbonate in carbonated water.

According to H. Reinsch, dolomite is not decomposed by boiling it with calcium sulphate and water, but if calcined dolomite is treated with carbon dioxide and again exposed to the action of calcium sulphate and water, F. Findeisen found that magnesium sulphate is formed. According to C. J. B. Karsten, dolomite behaves like magnesite towards an aq. soln. of *sodium chloride*, and it is not decomposed by an aq. soln. of *calcium chloride*. P. Berthier fused a mixture of four mols of *sodium carbonate* with one of dolomite, and on cooling obtained a clear mass with a crystalline fracture. If a very high temp. be employed carbon dioxide is evolved, and with a smaller proportion of sodium carbonate, the evolution of gas occurs as soon as the mixture begins to soften.

The so-called *hydrodolomite* or *hydromagnocalcite* found in stalagmitic and concretionary forms at Mt. Somma, Vesuvius, is a calcium magnesium carbonate with 6 to 17 per cent. water of hydration. R. Hermann [13] called a similar mineral *pennite*. C. U. Shepard found a variety which he called *hydronickel magnesite* tinted with nickel in Texas, Pa. A variety called *hydromanganocalcite* contains manganese. According to C. F. Rammelsberg, and F. von Kobell, hydrodolomite is really a mixture of hydromagnesite and dolomite. T. S. Hunt obtained what he regarded as a hydrated calcium magnesium carbonate, $CaCO_3.MgCO_3.5H_2O$, by the action of a small excess of sodium carbonate on a soln. containing equi-mol. proportions of magnesium and calcium chlorides. If this precipitate is kept in contact with sea-water for some days, it forms small transparent prismatic crystals; and by using insufficient sodium carbonate for complete precipitation, he obtained prismatic crystals of what he regarded as $7MgCO_3.10CaCO_3.21H_2O$.

It is difficult *to distinguish calcite from dolomite*. J. Lemberg [14] tried ferric chloride, and silver nitrate soln. The latter stains the two minerals unequally after ignition; and E. Hinden has stated that limestone is coloured reddish-brown by a soln. of ferric chloride,

and blue by a soln. of cupric sulphate, while dolomite is not affected—O. Mahler got poor results with ferric chloride, but good ones with the cupric sulphate. According to J. Lemberg, a soln. of aluminium chloride and hæmatoxylin or extract of logwood—*Lemberg's solution*—deposits a violet coating on calcite surfaces, but leaves dolomite uncoloured. F. Cornu has pointed out that if the powdered minerals are covered with water with a few drops of phenolphthalein, calcite gives an intense coloration while dolomite is not affected.

G. Bollmann allowed a soln. of calcium chloride or nitrate to act for 1–8 hrs. on hydrated magnesium carbonate at 120°–200°, but did not get any sign of the formation of dolomite, and he assumed that the reaction requires a long time ; on the other hand, he found that the formation of trihydrated **distrontium magnesium carbonate,** $2SrCO_3.MgCO_3.3H_2O$, proceeds more quickly when carbon dioxide is passed into a sat. soln. of strontium nitrate with magnesium carbonate in suspension, for 2 hrs. at 150°–170°. When the action is allowed to continue for a longer time, the product approximates to a *strontia-dolomite*, $SrCO_3.MgCO_3$. When a soln. of barium nitrate is treated in a similar manner, **barium magnesium carbonate,** $BaCO_3.MgCO_3$, is formed.

W. F. Foshag [15] groups the following minerals of the general formula $MgCO_3.5Mg(OH)_2.2R(OH)_3.4H_2O$, as **hydrotalcites.** C. Hochstetter, R. Hermann, C. U. Shepard, C. F. Rammelsberg, and W. R. Johnson described the mineral *hydrotalcite*, $MgCO_3.5Mg(OH)_2.2Al(OH)_3.4H_2O$. C. U. Shepard called it *houghite*, and R. Hermann, *völkernite* ; W. F. Petterd, L. K. Ward, L. Hezner, and A. Himmelbauer described *stichtite*, $MgCO_3.5Mg(OH)_2.2Cr(OH)_3.4H_2O$; L. J. Igelström, H. Sjögren, R. Mauzelius, and G. Flink, *pyroaurite*, $MgCO_3.5Mg(OH)_2.2Fe(OH)_3.4H_2O$; and E. Artini, and A. Pelloux, *brugnatellite*, $MgCO_3.5Mg(OH)_2.Fe(OH)_3.4H_2O$—but whose composition has not yet been definitely established. A comparison of the properties of these minerals is indicated in Table VIII.

TABLE VIII.—COMPARISON OF THE PROPERTIES OF THE HYDROTALCITES.

Hydrotalcite.	Pyroaurite.	Stichtite.	Brugnatellite.
White	Light brown	Lavender purple	Rose, light brown
Translucent	Translucent	Translucent	Translucent
Uniaxial	Uniaxial	Uniaxial	Uniaxial
Cleavage basal	Cleavage basal	Cleavage basal	Cleavage basal
Sp. gr. 2·04–2·09	Sp. gr. 2·07	Sp. gr. 2·12	Sp. gr.
n. 1·510	*n.* 1·55 (approx.)	*n.* 1·542	*n.* 1·533
Biref, weak	Biref. weak	Biref. 0·026	—
Pleochroism, none	Pleochroism, none	Very slightly pleochroic	Pleochroic

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§ 19. Magnesium Nitrates

The so-called *nitromagnesite* is said to occur as an efflorescent mass of hexahydrated magnesium nitrate besides the so-called nitrocalcite. A soln. of **magnesium nitrate,** $Mg(NO_3)_2$, is obtained by the action of nitric acid on magnesium carbonate, hydroxide, or oxide. As T. Graham [1] showed, when this soln. is evaporated on a water-bath, and cooled to ordinary temp. crystals of **hexahydrated magnesium nitrate,** $Mg(NO_3)_2.6H_2O$, are formed; but if the soln. be cooled below −20°, crystals of **enneahydrated magnesium nitrate,** $Mg(NO_3)_2.9H_2O$, appear. R. Funk found the transition point for the ennea- and hexa-hydrates to be −18°. The relation between these hydrates appears from the solubility curves. The following results by R. Funk refer to the **solubility** of the hexahydrated salt in grams per 100 grms. of sat. soln:

	−4·5°	0°	18°	40°	80°	90°	89°	77·5°	67°
$Mg(NO_3)_2$ . . .	39·50	39·96	42·33	45·87	53·69	57·81	63·14	65·67	66·55

where 90°, according to J. M. Ordway, represents the m.p. of the hexahydrate, and the succeeding numbers give a reversed curve. This means that soln. can be prepared with less water than is contained in the hexahydrate which occurs as the solid phase; and they can be regarded as soln. of the hexahydrate in the anhydrous salt. The numbers for the enneahydrate are likewise

	−7·8°	−20°	*c.* −29°	−23°	−20°	18°
$Mg(NO_3)$ . . .	15·00	27·4	34·6	35·44	36·19	38·03

where −18° is the transition point for the ennea- and hexa-hydrates, and the first two pairs in the series refer to the ice-line with the eutectic at *circa* −29°, according to F. Rüdorff. According to A. Ditte, if an aq. soln. of magnesium nitrate be heated carefully until a few gas bubbles begin to develop, the remaining colourless liquid is in a state of supersaturation at ordinary temp., and on shaking heat is developed, and crystals of **trihydrated magnesium nitrate,** $Mg(NO_3)_2.3H_2O$, are deposited. According to H. Lescœur, the same hydrate is formed from a sat. soln. of the nitrates mixed with an equal vol. of nitric acid; and he found that when the hexahydrate is heated to 65°, the vap. press. suddenly falls from 80 mm. to 25 mm., corresponding with the formation of the trihydrate. A. Ditte also claimed to have prepared short prismatic crystals of **dihydrated magnesium nitrate,** $Mg(NO_3)_2.2H_2O$, by heating the trihydrate a little above the m.p., but not sufficiently high for the evolution of red vapours; and dissolving the residue in monohydrated nitric acid which dissolves 5 per cent. of the salt at 2°, and 11 per cent. at 80°. The hot sat. soln. furnishes crystals of the dihydrate. A. Chodneff prepared this hydrate as a white hygroscopic powder by allowing the hexahydrate to stand over conc. sulphuric acid. R. Funk was unable to confirm the preparation of the dihydrate. Still further, T. Graham obtained what was regarded as **monohydrated magnesium nitrate,** $Mg(NO_3)_2.H_2O$, by heating the hexahydrate to 100°; and A. Ditte by heating magnesium nitrate until red fumes began to appear, dissolving the residue in as little hot monohydrated nitric acid as possible. Fine crystals of the monohydrate appear when the soln. is cooled.

According to A. Chodneff, the **crystals** of the hexahydrate belong to the triclinic system, but J. C. G. de Marignac found they are really monoclinic prisms, with axial ratios $a : b : c = 0{\cdot}5191 : 1 : 0{\cdot}9698$, and $\beta = 92° 56'$. L. Playfair and J. P. Joule gave 1·464 for the **specific gravity** of hexahydrated magnesium nitrate. F. Mylius and R. Funk found that at 18° a sat. soln. of magnesium nitrate contained 43·08 per cent. $Mg(NO_3)_2$, and had a sp. gr. 1·394. A. C. Oudemans gave for the sp. gr. of soln. containing

$Mg(NO_3)_2.6H_2O$.	1	5	10	20	30	40	45	49
Sp. gr. at 14° . .	1·0034	1·0202	1·0418	1·0869	1·1347	1·1909	1·2176	1·2397

Measurements have also been made by H. C. Jones, H. Schiff, by D. Dijken, and by

H. T. Barnes and A. P. Scott. The vol. of a soln. in 100 mols of H_2O at $\theta°$ between 0° and 60° was represented by N. S. Tschernay by the equation $v=1+0{\cdot}00015520\theta+0{\cdot}000003483\theta^2$. J. Wagner found the **viscosity** of N-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{8}N$-soln. of magnesium nitrate at 25° to be respectively 1·1706, 1·0824, 1·0396, and 1·0198. Measurements were also made by S. Arrhenius, and K. Mützel. A. Strickler and J. H. Mathews studied the electric endosmose of magnesium nitrate.

According to A. Chodneff, the crystals of the hexahydrate lose 28·25 per cent.—nearly two-thirds—of water of crystallization when confined over conc. sulphuric acid ; and he stated that the **melting point** of the hexahydrate is 100° ; J. M. Ordway, and W. A. Tilden gave 90°. A. Chodneff found that the hexahydrate loses 34·14 per cent. of water at its m.p. and congeals to a glass-like mass. A. Chodneff found that the percentage loss on calcination :

	110°–115° (6 hrs.)	115°–120° (6 hrs.)	120°–125° (23 hrs.)	140°–150° (28 hrs.)	150°–155° (6 hrs.)	210° (5 hrs.)
Loss	20·87	28·97	31·05	34·72	35·10	35·32

T. Graham was unable to drive off all the water at 400°, and at a dull red heat it loses the remainder of the water, and at the same time gives off nitrogen peroxide and oxygen. D. Gernez found that in air free from carbon dioxide, nitric acid is given off when magnesium nitrate is heated to 150° ; and J. C. G. de Marignac found the crystals to be stable in dry air.

According to A. Ditte, when trihydrated magnesium nitrate is melted and heated to the temp. at which red fumes are evolved, and the product leached with water, **magnesium trioxynitrate,** $3MgO.Mg(NO_3)_2$, remains as white tabular crystals. A. Chodneff heated the hexahydrate with stirring until the mass melted and lost all its water. The product was washed with water, and there remained a white basic nitrate, **magnesium dioxynitrate,** $2MgO.Mg(NO_3)_2$, which is insoluble in alcohol and water, but soluble in acids. There is really nothing to establish the individuality of those, although G. Didier made crystals of **pentahydrated magnesium dioxynitrate** by dissolving 200 grms. of hexahydrated magnesium nitrate in 150 c.c. of water at 100°, and adding 10 grms. of magnesia prepared at a low temp. —350°–400°. The temp. is gradually raised to 150° and the filtrate, preserved in a closed vessel, deposits a flocculent precipitate in a few days. The precipitate is isolated by suction and press. keeping it as much as possible out of contact with the carbon dioxide of the atm. The microscopic crystals consist of doubly refracting needles which are rapidly decomposed by cold water or absolute alcohol, with the separation of magnesium hydroxide.

J. C. G. de Marignac found for the **specific heat** of a soln. of a mol of $Mg(NO_3)_2$ in n mols of water, between 21° and 52°,

n	15	25	50	100	210
Sp. ht.	0·6777	0·7568	0·8517	0·9145	0·9537
Mol. ht.	283·7	453	893	1782	3575

H. C. Jones and co-workers measured the lowering of the **freezing point** of aq. soln. of magnesium nitrate and found for soln. with 1·142, 0·921, and 32·07 grms. of $Mg(NO_3)_2$ per 100 grms. of water, the f.p. were respectively —0·370°, —3·559°, and —22·500°, and the mol. lowering of the f.p. respectively 4·8°, 5·75°, and 10·40°.

According to J. Thomsen, the **heat of formation,** $(Mg, O_2, N_2O_4, 6H_2O)=214·53$ Cals. ; and, according to M. Berthelot, $Mg(OH)_2+2HNO_{3aq.}=27·6$ Cals. J. Thomsen gave —4·22 Cals. for the **heat of solution** of a mol of the hexahydrate in 400 mols of water, and S. U. Pickering, —4·547 ; the latter found 0·936 Cal. for the heat of soln. in alcohol. D. Dijken found the following difference in the **refractive indices** of the soln. and water for a mol. of $Mg(NO_3)_2$ in v litres of water between 15° and 16·5° :

v	1	4	16	32	64	128
Diff.	0·012258	0·003086	0·0007890	0·0003982	0·0001991	0·0001020

According to C. Chéneveau, the value of $(\mu_D-1)D$ in dil. soln., decreases with the

press. of the solute. W. N. Hartley found that the **absorption spectrum** for a soln. with 256·4 grms. per litre, and thickness 4 mm., gave bands λ^{-1}, 3069 to 3772; and for a thickness 2 mm., absorption bands for λ^{-1}, 3069 to 3772; and for a thickness 2 mm., absorption bands for λ^{-1}, 3149 to 3504. J. R. Collins measured the ultra-red absorption spectrum of aq. soln. of the nitrate. F. Kohlrausch and L. Holborn give for the **equivalent conductivity,** λ, of magnesium nitrate, at 25°; H. C. Jones gives for the mol. conductivity, μ, at 0°, the percentage **ionization** α, and the temp. coeff., k, of soln. of a mol of the salt in v litres of water at 0°:

v	8	32	64	128	256	512	1024
λ (25°)	—	104·6	111·0	115·7	119·0	122·9	125·6
μ (0°)	88·91	101·55	110·78	119·01	120·68	123·34	122·89
α (0°)	72·1	82·4	89·9	96·5	97·9	100·0	99·7
k (0°–12·5°)	2·76	3·23	3·58	3·74	3·97	3·99	4·06

C. A. Kraus and J. E. Bishop measured the conductivity of soln. of magnesium nitrate in mixtures of propyl alcohol and water. A. Chassy gave data for the **transport numbers** of the ions.

J. W. Thomas found that **hydrogen chloride** reacts vigorously with heated magnesium nitrate and red fumes of nitrogen perioxide are evolved. T. Graham found the hydrates of magnesium nitrate are all hygroscopic, and readily soluble in **alcohol,** and he found that a hot sat. soln. of anhydrous magnesium nitrate, in alcohol, forms a double compound $Mg(NO_3)_2.4\frac{1}{2}C_2H_5OH$; and A. Chodneff represented the composition $Mg(NO_3)_2.3C_2H_5OH$. E. C. Franklin and C. A. Kraus found magnesium nitrate to be soluble in **liquid ammonia,** and the soln. immediately gives a precipitate with ammonium chloride; one is formed more slowly with ammonium bromide, and none at all with ammonium iodide; ammonium sulphide gives a precipitate of $(NH_4)_2.S.2MgS.nNH_3$; ammonium chromate, and borate also give precipitates with the liquid ammonia soln. of magnesium nitrate. D. N. Jackman and A. Browne studied the ternary systems, $Mg(NO_3)_2$—$NaNO_3$—H_2O, and $MgSO_4$—$Mg(NO_3)_2$—H_2O, at 25°, and found that no double salts or solid soln. are formed.

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§ 20. Magnesium Orthophosphates

Analyses of the guano mineral *bobierrite* or *hautefeullite* from Chile by A. Lacroix,[1] and from Bambe by L. Michel, show that it has a composition corresponding closely to that required for normal **hexahydrated magnesium orthophosphate,** $Mg_3(PO_4)_2.8H_2O$. According to C. Stein and B. Tollens, it also separates from pathological and form normal urine ; small quantities have also been reported in the cereals, in bones, in urinary calculi, and in the intestinal concretions of some animals. T. Graham,[2] and W. Gregory prepared what has been regarded as hydrated normal magnesium phosphate, $Mg_3(PO_4)_2$, by treating a soln. of magnesium sulphate with normal sodium phosphate ; the precipitate dried at 100° contains the eq. of $5H_2O$. C. Stein and B. Tollens used disodium hydrophosphate, and employed as well conc. soln. made slightly alkaline with sodium hydrocarbonate. A crystalline precipitate forms in 12–24 hrs. K. Kraut recommended mixing magnesium sulphate or chloride with a mixed soln. of disodium hydrophosphate, or of disodium hydrophosphate and borax, the flocculent precipitate soon becomes crystalline. L. Schaffner boiled magnesium hydrophosphate repeatedly with water so long as this acquired an acid reaction, and obtained the normal phosphate ; and H. Debray heated the same compound with water in a sealed tube at 120°. G. A. Daubrée prepared rhombic plates of magnesium phosphate by heating magnesium oxide in an atm. of phosphorus pentachloride : $8MgO+2PCl_5=Mg_3(PO_4)_2+5MgCl_2$. A. de Schulten mixed a soln. of 20 grms. of heptahydrated magnesium sulphate in two litres of water and cooled at 10°, with a soln. of 19·4 grms. of dodecahydrated disodium hydrophosphate and 4 grms. of sodium hydrocarbonate in a litre of water, and, after diluting the mixture with a litre of water, allowed it to stand at 20°–25° for a long time. Crystals of bobierrite were slowly formed. He also obtained crystals without using the sodium hydrocarbonate.

Bobierrite occurs in colourless and white needles. A. de Schulten found the artificially prepared **crystals** of the octohydrate, $Mg_3(PO_4)_2.8H_2O$, to be monoclinic prisms, with axial ratios $a : b : c=0·076 : 1 : 0·74$, and β is about 106°. A. Sachs supposed bobierrite to be isomorphous with vivianite and symplesite. A. Lacroix gave 2·41 for the **specific gravity** of bobierrite, and A. de Schulten, 2·195 at 15°, for the artificial product. The latter also found that the synthesized octohydrate did not lose its water of crystallization at 100°, while the hydrated precipitate lost about 82 per cent. of its water at 100°, and still more with a prolonged heating. According to K. Kraut, if precipitated magnesium phosphate be dried over conc. sulphuric acid, the product contains 43·8 per cent. of water ; if at 100°, 10·86 per cent. ; and if calcined at a red heat 4·77 per cent. of water. L. Schaffner found a very small loss at 100°, a loss of 23 per cent. at 180°, and a further loss of 9·10 per cent. at a red heat, and his analysis of the original phosphate corresponded with $Mg_3(PO_4)_2.7H_2O$; C. Stein and B. Tollens' and H. Debray's analyses of the crystals corresponded with $Mg_3(PO_4)_2.5H_2O$; C. Stein and B. Tollens, and K. Kraut's analyses of the air-dried precipitate, with $Mg_3(PO_4)_2.22H_2O$; and A. de Schulten's analysis of artificial bobierrite, with $Mg_3(PO_4)_2.8H_2O$. Both T. Graham, and W. Gregory found that the phosphate has a **melting point** near a white heat, and the resulting clear glass is easily soluble in acids. According to M. Berthelot, the **heat of formation** of colloidal normal magnesium phosphate from its elements is 910–6 Cals. ; and from magnesium sulphate and normal sodium phosphate is compounded of two factors—the initial formation of an amorphous precipitate, 4·86 Cals., followed by its transformation into crystals which in 5–6 mins. liberate 8·12 Cals. With magnesium chloride, the numbers are respectively −4·44 Cals. and 12·18 Cals. The **heat of neutralization** is $Mg(OH)_2+H_3PO_4aq.=Mg_3(PO_4)_2aq.$ +57·80 Cals. for the amorphous, and 83·00 Cals. for the crystalline precipitate. Bobierrite has a positive **double refraction.**

According to F. K. Cameron and J. M. Bell, the behaviour of the magnesium phosphates in contact with **water** is quite similar to that of the calcium phosphates,

A. Lacroix found bobierrite to be insoluble in water, while J. A. Völcker stated that a litre of water dissolves in 7 days 0·205 grm. of the freshly precipitated normal phosphate, and 0·100 grm. of the calcined. J. von Liebig found a litre of water containing 2 grms. of **sodium chloride** dissolves 75·8 mgrms. of the precipitated phosphate ; and a litre of water with 3 grms. of sodium nitrate dissolves 61·9 mgrms. According to A. Lacroix, bobierrite is soluble in **nitric acid,** and, according to L. Schaffner, normal magnesium phosphate is easily soluble in **acetic acid.** According to B. W. Gerland, when normal magnesium phosphate is suspended in water, it rapidly absorbs **sulphur dioxide,** and forms an oily liquid ; if an excess of the phosphate is present it does not alter its composition. A soln. containing a mol of $Mg_3(PO_4)_2$ and 4·3 mols of sulphur dioxide furnishes crystals of trihydrated magnesium hydrophosphate when allowed to stand in vacuo, and a similar product, but less hydrated, is gradually deposited in needle-like crystals on adding sodium carbonate ; or on boiling the soln. According to L. Grandeau, a double alkali magnesium phosphate is produced when the phosphate is fused with an **alkali sulphate,** but no magnesium oxide is formed. E. Erlenmeyer has shown that an acid **ammonium citrate** soln. dissolves normal magnesium phosphate quite readily, but not so readily in a neutral citrate soln. A. Chizynsky studied the distribution of phosphoric acid between magnesium and **calcium salts.**

According to L. B. G. de Morveau, magnesium oxide forms a white vitrifiable substance when ignited with two parts of sodium ammonium phosphate. J. J. Berzelius also noted the solubility of magnesia in fused sodium ammonium phosphate before the blowpipe. H. Rose also made a **sodium magnesium phosphate,** $NaMgPO_4$, by fusing equimolar parts of magnesium pyrophosphate with sodium carbonate ; the analysis corresponded with $3MgO.3Na_2O.2P_2O_5$. L. Ouvrard obtained a substance with the same composition by fusing normal sodium phosphate with magnesium oxide, and extracting the slowly cooled mass with water. The dendritic crystals have a sp. gr. 2·5 at 20°, and they are doubly refracting. H. Rose made anhydrous **potassium magnesium phosphate,** $KMgPO_4$, by calcining a mixture of magnesium pyrophosphate and potassium carbonate. R. Weber's analyses of a similar product were found by H. Rose to be too low in alkali for $KMgPO_4$, but H. Rose pointed out that R. Weber washed the material with ammoniacal water which by hydrolytic decomposition removed the alkali and left magnesium hydrophosphate behind. L. Grandeau obtained the same compound by heating for many hours at 800° an intimate mixture of magnesium pyrophosphate with 25 times its weight of potassium sulphate, and extracting the cold mass with hot water. A white powder consisting of needle-like crystals remained. According to L. Ouvrard, potassium pyrophosphate or orthophosphate yields rhombic prisms of the salt P_2O_5, 2MgO, K_2O, previously described by L. Grandeau. Magnesium phosphate yields the same products as the oxide, but the chloride yields a chlorophosphate unless the alkaline phosphate is present in considerable excess. L. Ouvrard's potassium magnesium phosphate had a sp. gr. 2·6 at 20°, and was easily soluble in acids. H. Erdmann and P. Köthner prepared **hexahydrated rubidium magnesium phosphate,** $RbMgPO_4.6H_2O$, by mixing soln. of magnesium sulphate and of rubidium phosphate. The crystalline precipitate is not decomposed by boiling water, and it is soluble in cold dil. hydrochloric acid.

M. Berthelot, and A. Quartaroli studied the equilibrium conditions between phosphoric acid, magnesium oxide, and the alkali hydroxides. The latter found that the behaviour of the magnesium oxide is different from that of barium or calcium oxides. Thus, on adding one eq. of magnesia and two eq. of sodium hydroxide to one mol of phosphoric acid, only magnesium oxide is precipitated, whilst if the sodium hydroxide is replaced by potassium hydroxide, a portion of the latter passes into the insoluble state. On adding one eq. of sodium or potassium hydroxide to monomagnesium phosphate, the amount of phosphoric acid precipitated is much less than in the other cases and only amounts to about one-sixth of the total quantity ; seeing that dimagnesium phosphate, like the dicalcium salt,

is only very slightly soluble and that the alkali hydroxide present is sufficient to precipitate it, it is probable that soluble double phosphates are formed. M. Schröcker and M. Violet prepared **enneahydrated sodium magnesium phosphate,** $NaMgPO_4.9H_2O$, by heating a soln. of equimolar parts of phosphoric acid and sodium carbonate until carbon dioxide is expelled, and to the cold soln., adding magnesia, which has been heated to the lowest possible temp., until the liquid has a neutral reaction. After the mixture has stood some days, microscopic prisms are formed which are freed from the mother liquid by press. The crystals belong to the triclinic system, and, according to K. Haushofer, they have the axial ratios $a:b:c=1{\cdot}2588:1:1{\cdot}4380$, and $\alpha=89°\ 42'$, $\beta=93°\ 13'$, $\gamma=89°\ 31°$. M. Schröcker and M. Violet prepared **hexahydrated potassium magnesium phosphate,** $KMgPO_4.6H_2O$, in a similar manner; K. Haushofer found the crystals belong to the rhombic system and have the axial ratios $a:b:c=0{\cdot}5584:1:0{\cdot}9001$. The crystals lose five-sixths of their water at 100°, and they are decomposed by water. A. Metz obtained crystals of this double salt by adding potassium carbonate to beer.

K. Haushofer prepared an acid double phosphate which he regarded as decapentahydrated *potassium dimagnesium hydrodiphosphate*, but did not describe the method; he said that the crystals were triclinic plates with axial ratios and angles $a:b:c=0{\cdot}9418:1:0{\cdot}5003$, and $\alpha=90°\ 7'$, $\beta=92°\ 4'$, and $\gamma=95°\ 48'$. L. Chevron and A. Droixhe prepared crystals of what they regarded as acid phosphates: $K_2O.4MgO.2P_2O_5.7H_2O$, and $K_2HMg_3(PO_4)_3.4\frac{1}{2}H_2O$, from mixtures of soln. of potassium dihydrophosphate, potassium hydrocarbonate, and magnesium sulphate of different conc.; but there is no evidence of the chemical individuality of the products.

Crystals of **hexahydrated ammonium magnesium phosphate,** $Mg(NH_4)PO_4.6H_2O$, were found by G. L. Ulex [3] in some old soil, under quantities of cattle dung, in the neighbourhood of Hamburg, and the mineral was called *struvite*, after a Russian statesman; and E. F. Teschemacher called it *guanite*. F. de la Provostaye found the mineral in guano from Patagonia, and it has been reported in guano from other localities. E. P. Pittman, R. W. E. MacIvor and G. vom Rath reported it in the bat guano from the Skipton Caves (Victoria); H. Ludwig found it in intestinal concretions; and it is deposited from decomposing urine. O. B. Böggild found crystals of struvite in extracts from fossil plants; peat extracts, etc.

A. F. de Fourcroy first made the salt by treating magnesium phosphate with ammonium hydrophosphate; J. J. Berzelius mixed a neutral magnesium salt with ammonium hydrophosphate. In both these cases, G. F. Wach found the soln. becomes acidic. L. Blum also preferred sodium phosphate as precipitating agent because the precipitate settles more quickly; while C. Mohr, and W. Gibbs preferred sodium ammonium phosphate because it precipitates more rapidly and completely. A. Riffault mixed a magnesium salt first with ammonium carbonate, and then with disodium hydrophosphate. According to C. A. Lesueur, magnesium hydroxide or carbonate is transformed into ammonium magnesium phosphate when it is allowed to stand in contact with a soln. of ammonium hydrophosphate; and likewise also when magnesium hydrophosphate is treated with aq. ammonia, ammonium sulphide, or ammonium carbonate; C. Stein, and B. Tollens observed a similar result with normal magnesium phosphate. J. W. C. Davis also prepared this salt. A. de Schulten obtained good crystals of the double salt by mixing a soln. of 28 grms. of diammonium hydrophosphate, 10 grms. of ammonium sulphate, and 12 grms. of phosphoric acid in 80 c.c. of water with a soln. of 16 grms. of heptahydrated magnesium sulphate in 20 c.c. of water. Comparatively large crystals were produced by H. Vohl, O. Richter, and E. Monier by slowly mixing the soln. separated by a permeable diaphragm. A. Millot and L. Maquenne obtained large crystals in acid or neutral soln. in the presence of ammonium citrate; and K. Haushofer from a soln. of the double phosphate in ammonium citrate. R. H. Solly, and A. Arzruni have reported the formation of crystals of struvite in certain culture media for bacteria, and in peptone soln.

M. Berthelot has studied the equilibrium between soln. of magnesium chloride,

and of ammonium phosphate. Hexahydrated magnesium ammonium phosphate is precipitated whenever a neutral magnesium salt is brought in contact with a soln. containing ammonia and phosphoric acid. According to J. J. Berzelius, the salt is slowly precipitated, and the precipitation is never complete unless an excess of phosphate is present in the soln. W. H. Wollaston noticed that the precipitate is deposited on the sides of the glass containing vessel, especially where the stirring rod has scratched it. This salt is usually the form in which magnesium is precipitated in analytical work, and reciprocally also, it is often the form in which phosphoric acid is precipitated. According to H. Neubauer, the precipitation is practically complete even in the presence of comparatively large quantities of ammonium salts, but the composition of the precipitate is largely determined by the nature of the soln., *e.g.* (i) the precipitate contains a lower proportion of magnesium than the normal phosphate in neutral and ammoniacal soln.; (ii) the precipitate has the normal composition if an excess of the magnesium salt is present; and (iii), the precipitate contains more magnesium than the normal phosphate in the presence of an excess of both magnesium salt and ammonia. R. Reidenbach believes the third observation is not correct, and that the precipitate contains less, not more, magnesium than the normal phosphate.

A. Gawalowsky obtained large crystals with the composition $(NH_4)_2O.\frac{1}{2}MgO.2P_2O_5.24H_2O$, by crystallization from a soln. of the normal phosphate in acetic acid. The analyses of C. Lindbergson led J. J. Berzelius to assume that another ammonium magnesium phosphate exists containing less magnesium than $NH_4MgPO_4.6H_2O$; and J. Tünnermann supposed the existence of even six varieties of this salt, but T. Graham and G. F. Wach showed that there is only one double magnesium ammonium phosphate. F. A. Gooch and M. Austin have confirmed the existence of a compound $(NH_4)_2H_2Mg(PO_4)_2.2H_2O$, whose production is favoured by the presence of an excess of a soluble phosphate or of ammonium salts in the soln. R. W. E. MacIvor reported three minerals in the bat guano of the Skipton Caves (Victoria)—*hannayite*, $Mg_2H_2(PO_4)_2.MgH_2(NH_4)_2(PO_4)_2.8H_2O$, in triclinic crystals with $a:b:c=0{\cdot}6990:1:0{\cdot}9743$; *schertelite*, $Mg(NH_4)_2H_2(PO_4)_2.4H_2O$, in small ill-defined crystals; and *dittmarite*, $Mg(NH_4)PO_4.2MgH_2(PO_4)_2.8H_2O$, in rhombic crystals. H. Neubauer and K. Bube also inferred that a compound *magnesium tetrammonium diphosphate*, $Mg(NH_4)_4(PO_4)_2$, *i.e.* $(NH_4)_3PO_4.Mg(NH_4)PO_4$, is formed in neutral or ammoniacal soln. because, when the precipitate is ignited, some phosphoric acid is volatilized, which is not the case when the normal double salt is ignited under similar conditions. It is assumed that during the ignition of the tetrammonium salt, magnesium metaphosphate is first formed: $Mg(NH_4)_4(PO_4)_2 \rightarrow Mg(PO_3)_2+4NH_3+2H_2O$; and that on further ignition, the metaphosphate decomposes into pyrophosphate and volatile phosphoric oxide: $2Mg(PO_3)_2 \rightarrow Mg_2P_2O_7+P_2O_5$.

Disturbances also arise in the presence of alkali salts, so that it is usual to dissolve the precipitate in dil. nitric acid, and reprecipitate it from a soln. which will give the normal phosphate, $NH_4MgPO_4.6H_2O$. Many other observations have been made on this subject by W. Heintz, F. G. Jörgensen, C. Stünkel, T. Wetzke, and F. Wagner, O. Popp, T. R. Ogilvie, E. W. Parnell, W. Kubel, L. Brünner, etc.

Struvite is sometimes colourless, or it may have a yellowish or brownish tinge. K. Haushofer established the identity of the **crystals** of struvite and of hexahydrated ammonium magnesium phosphate. According to A. Sadebeck, the pyramidal crystals belong to the rhombic system, and have axial ratios $a:b:c=0{\cdot}5667:1:0{\cdot}9121$. H. Haga and F. M. Jäger have studied the **X-radiograms** of crystals of struvite. E. F. Teschemacher gave 1·65 for the **specific gravity** of struvite; O. B. Böggild, 1·715; A. de Schulten, 1·711. The **hardness** is about 2 on Mohs' scale. M. Berthelot gave for the **heat of formation** of crystalline ammonium magnesium phosphate $MgNH_4PO_4$ from its elements as 898·8 Cals. The crystals of struvite have a positive **double refraction,** and, according to O. B. Böggild, the **indices of refraction** are $\mu_\alpha=1{\cdot}4954$, $\mu_\beta=1{\cdot}4963$, and $\mu_\gamma=1{\cdot}5043$. K. Bube measured the **electrical conductivities** of aq. soln. of mono- and hexa-hydrated magnesium ammonium phosphate at different temp. K. Hausmann, and E. Kalkowsky have studied the **pyroelectrical effects** produced by the crystals.

According to C. H. Pfaff, hexahydrated ammonium magnesium phosphate loses ammonia when exposed to air at ordinary temp.; and, according to G. F. Wach,

it loses both water and ammonia when dried for several days in vacuo over conc. sulphuric acid. T. Graham reported that when heated to 100°, in a retort, it loses five-sixths of its water of crystallization but no ammonia, while H. Struve maintained, on the contrary, that some ammonia is evolved; L. Chevron and A. Droixhe stated that the residue left on drying at 100° is $\frac{3}{4}NH_3.2MgO.P_2O_5.2\frac{1}{6}H_2O$. P. Griessmayer reported that the hexahydrate loses some ammonia when boiled with water.

K. Bube found the transition temp. for the conversion of the hexahydrate to **monohydrated ammonium magnesium phosphate,** $Mg(NH_4)PO_4.H_2O$, under water is between 48° and 49°; and under its own mother liquid, between 56° and 57°. A. Millot and L. Maquenne boiled equimolar proportions of $MgSO_4$ and $(NH_4)_2HPO_4$, and found that the normal phosphate, $Mg_3(PO_4)_2$, is first formed, and that this then takes up ammonia and water, forming plates and cubes of the monohydrate, $Mg(NH_4)PO_4.H_2O$. The crystals are not doubly refracting, they remain unchanged at 100°, and dissolve neither in water nor in a soln. of ammonium citrate.

According to A. F. de Fourcroy and J. J. Berzelius, when hexahydrated ammonium magnesium phosphate is strongly heated, it loses all its ammonia and water and is reduced to a powder which fuses at a higher temp. forming a clear glass of magnesium pyrophosphate; if, when all the water and ammonia have been expelled at a moderate heat, the residue be subsequently exposed to a greater degree of heat, it becomes slightly incandescent in consequence of an intramolecular change—according to O. Popp, owing to the passage of the pyrophosphate from a crystalline to an amorphous condition—because no change in weight can be detected before and after the material has glowed. H. Struve, and O. Popp found that the incandescence occurs if the magnesium pyrophosphate be contaminated with calcium or other magnesium compounds, and, particularly so, with silica. Analyses confirmatory of the conversion of the double salt into magnesium pyrophosphate: $2Mg(NH_4)PO_4.6H_2O \rightarrow Mg_2P_2O_7+2NH_3+13H_2O$, were made by G. F. Wach, A. Riffault, C. Lindbergson, J. J. Bergson, F. Stromeyer, C. H. Pfaff, etc. The hexahydrated magnesium ammonium phosphate precipitated in analysis is weighed as magnesium pyrophosphate.

J. J. Berzelius said that hexahydrated ammonium magnesium phosphate is slightly soluble in water, and C. R. Fresenius found that a litre of **water** at 10° dissolves 0·065 grm. of ammonium magnesium phosphate. E. Ebermayer gave 0·074 grm. per litre at 20·5°–22·5°; J. von Liebig gave 0·107 grm.; and J. A. Völcker, 0·106 grm. P. Wenger gave for the solubility of NH_4MgPO_4 in grams per litre at different temp.:

	0°	20°	40°	50°	60°	70°	80°
NH_4MgPO_4	0·023	0·052	0·036	0·030	0·040	0·016	0·019

The irregularity in the results shows that equilibrium was not attained. The results are also probably complicated by hydrolysis, and by the transition from the hexa- to the mono-hydrate. K. Bube also measured the solubility of the mono- and hexa-hydrates in water. The double salt is much less soluble in water containing *ammonia*, thus, C. R. Fresenius found a litre of an aq. soln. of ammonia dissolves 0·0226 grm. of the double salt; while, according to F. G. Jörgensen, the solubility of the double salt in 2½ per cent. aq. ammonia is approximately eq. to 0·0006 grm. MgO per litre; and, according to C. Stünkel, T. Wetzke, and F. Wagner aq. soln. of 1, 2, and 3 per cent. ammonia dissolve respectively the eq. of 0·00050, 0·00023, and 0·00008 grm. of MgO. E. Ebermayer found that between 20·5° and 22·5°, a litre of aq. ammonia dissolves:

Per cent. NH_3	0	1·98	2·48	4·95	6·64	7·43	9·91
Grm. $(NH_4)MgPO_4$	0·0741	0·0322	0·0272	0·0232	0·0221	0·0191	0·0164

The solubility increases with rise of temp. Expressing the results in grams of NH_4MgPO_4 per 1000 grms. of a mixture of one part aq. ammonia (sp. gr. 0·96) and 4 parts of water, P. Wenger found:

	0°	20°	40°	50°	60°	70°	80°
$(NH_4)MgPO_4$	0·087	0·098	0·136	0·153	0·174	0·178	0·145

The decrease in the solubility at the higher temp. may be connected with the transition from the hexa- to the mono-hydrate. C. R. Fresenius found the double salt is more soluble in the presence of 20 per cent. *ammonium chloride*, for a litre of the soln. dissolved 0·132 grm. of the double salt. F. G. Jörgensen also noted that the solubility of the double salt is increased in the presence of ammonium chloride, so that a litre of 2½ per cent. ammonia with a gram of ammonium chloride dissolves the eq. of 0·013 grm. of MgO. P. Wenger gives for the solubility of the double salt in a 5 per cent. soln. of ammonium chloride, in grams of NH_4MgPO_4 per 1000 grms. of solvent:

	0°	20°	30°	40°	50°	60°	70°	80°
NH_4MgPO_4 . .	0·60	1·05	1·13	0·71	0·93	1·73	1·24	1·91

Here again there is every indication that equilibrium was not attained. When the ammonium chloride soln. of the double salt is boiled, K. Kraut found that ammonia is evolved. According to C. R. Fresenius, a litre of a soln. of ammonium chloride and ammonia dissolved 0·064 grm. of the double salt; P. Wenger from 100 grms. of a 5 per cent. soln. of ammonium chloride with 4 of ammonia per 100 dissolved 0·165 and 0·274 grm. per litre at 20° and 60°. P. Wenger's values for the solubilities of the double salt in a 5 per cent. soln. of *ammonium nitrate* resemble those with ammonium chloride:

	0°	20°	30°	40°	50°	60°	70°	80°
NH_4MgPO_4 . .	1·10	0·46	0·54	0·64	0·72	0·85	0·83	1·01

J. von Liebig found that an aq. soln. of *ammonium sulphate* containing 2·2, 3·0, and 10 grms. $(NH_4)_2SO_4$ per litre, dissolved respectively 0·0717, 0·1130, and 0·147 grm. of the double salt. A. Bolis found that 2 grms. of hexahydrated ammonium magnesium phosphate in contact with 100 c.c. of a soln. of *ammonium citrate* (400 grms. citric acid per litre) loses, by soln., 0·457 per cent. in weight at ordinary temp., and 0·587 per cent. at 50°. A. Millot found a boiling soln. of ammonium citrate dissolves the double salt, which re-crystallizes out on cooling. J. Ville noted that a soln. of ammonium citrate dissolves only traces of the double salt, while soln. of *calcium citrate* dissolve larger amounts. J. von Liebig found that water containing 2 grms. of *sodium chloride* per litre dissolves 0·1234 grm. of the double salt per litre, and an aq. soln. containing 3 grms. of *sodium nitrate* per litre dissolves 0·0931 grm. of the double salt. When the double salt is precipitated in the presence of alkali salts, the latter are occluded or adsorbed and the resulting increase in weight more than counterbalances the solubility losses.

Hexahydrated ammonium magnesium phosphate is readily soluble in **acetic acid** and in other dil. acids, and, as C. H. Pfaff showed, the dissolution is accompanied by partial decomposition. J. von Liebig found a litre of water sat. with **carbonic acid** dissolves 1·425 grms. of the double salt; B. W. Gerland studied the solubility of the double salt in **sulphurous acid.** According to A. Marcet, a soln. of the double salt in **hydrochloric acid,** when evaporated to dryness and heated, furnishes a sublimate of ammonium chloride. When digested with **glycerol,** especially at an elevated temp., the ammonium double salt is converted into magnesium hydrophosphate. According to M. Märcker, and P. Griessmayer, when the double salt is boiled with magnesium oxide, part of the ammonia is expelled; and C. H. Pfaff found that the **fixed alkalies** liberate ammonia from the double salt, although H. Rose found the salt is but incompletely decomposed by **alkali carbonates.** C. H. Pfaff found that when ignited with **carbon,** some phosphorus is evolved. H. Struve, and R. Weber found that when ignited in the presence of **reducing agents**—*e.g.* carbon, hydrogen, unburnt gases from the source of heat, etc.—at a high temp., phosphorus, phosphorus oxide, or hydride are evolved, and, as shown by W. C. Heraeus, W. P. Headden, etc., these vapours attack the platinum crucible.

A rare mineral found in the quartz and clay slate of Höllgraben in Salzburg (Austria), and having a superficial resemblance to topaz,[4] was shown by J. N. von Fuchs to be a magnesium fluophosphate, and was named *wagnerite*. A. Breithaupt

called it *pleuroclase*. Analyses by J. N. von Fuchs, and C. F. Rammelsberg are in agreement with the formula, $Mg_3(PO_4)_2.MgF_2$. P. Groth regards it as a salt of orthophosphoric acid, $Mg(MgF)PO_4$; and G. Tschermak as a salt of HMg_2PO_4, namely, $Mg_2F.PO_4$, in which the hydrogen can be replaced by fluorine :

Monoclinic crystals, with a composition approximating to wagnerite, were found by A. Scacchi near Massa di Somma and San Sebastiano (Vesuvius), and regarded as a distinct mineral species which was called *cryphiolite;* but F. Zambonini showed that cryphiolite and wagnerite are really the same. F. von Kobell found a mineral at Kjerulfin, near Bambe (Norway), which he regarded as $2Mg_3(PO_4)_2.CaF_2$, and named *kjerulfine*, but G. C. Wittstein, M. Bauer, and W. C. Brögger and E. Reusch showed that the optical properties of kjerulfine are identical with those of wagnerite, and this conclusion is in agreement with analyses by F. Pisani, C. F. Rammelsberg, F. Friederici, etc. It is probable that calcium can replace magnesium in wagnerite, forming *calcium-wagnerite*, and these have been synthesized by H. St. C. Deville and H. Caron, etc. H. Winter prepared *strontium-wagnerite* and *barium-wagnerite*. H. St. C. Deville and H. Caron also prepared *chloro-wagnerite* in which the fluorine is replaced by chlorine; and *ferro-wagnerite* and *mangano-wagnerite*, where ferrous oxide and manganous oxide respectively replace the magnesium oxide of normal wagnerite. A. Ditte has made an analogous series of *bromo-wagnerite;* while H. Debray, and H. Lechartier prepared *arsenico-wagnerite*, and P. Hautefeuille, *vanadium wagnerite*.

In H. St. C. Deville and H. Caron's synthesis of normal wagnerite, 132 parts of ammonium dihydrophosphate and 60 parts of magnesium fluoride were heated with a great excess of magnesium chloride in a carbon crucible at a red heat. The soluble matter was leached with water from the cold mass; by fusing one part of calcium fluoride with ten parts of normal magnesium phosphate and a large excess of calcium chloride, calcium chloro-wagnerite was formed: $(Ca, Mg)_3(PO_4)_2.(Ca, Mg)(F, Cl)_2$. H. Winter made wagnerite by melting equimolar parts of normal magnesium phosphate and magnesium fluoride.

The colour of wagnerite is yellowish- or reddish-white. The prismatic **crystals** are holohedral, and belong to the monoclinic system with axial ratios $a : b : c = 1{\cdot}9145 : 1 : 1{\cdot}5059$, and $\beta = 71° 53'$. The **specific gravity** is 3·07 to 3·15; J. N. von Fuchs gave 3·13 at 15°; C. F. Rammelsberg, 3·026 at 15°; F. Pisani, 3·12; F. von Kobell, 3·15; and H. St. C. Deville and H. Caron, 3·12 for artificial wagnerite. The **hardness** is 5 to $5\frac{1}{2}$. Wagnerite fuses in the blowpipe flame to a grey glass. The **double refraction** is negative; the dispersion feeble; and, according to M. Levy and A. Lacroix, the **indices of refraction** are $\alpha = 1{\cdot}569$; $\beta = 1{\cdot}570$; and $\gamma = 1{\cdot}582$. The mineral is soluble in nitric and hydrochloric acids.

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§ 21. Magnesium Hydrophosphates

Anhydrous magnesium hydrophosphate, $MgHPO_4$, has not been made, but four hydrates have been reported, $MgHPO_4.nH_2O$, where n is 1, 3, $4\frac{1}{2}$, or 7. Magnesium hydrophosphate occurs in human fæces; and trihydrated magnesium hydrophosphate occurs as a guano mineral, *newberyite*. A specimen of the latter from the bat guano in the Skipton Caves (Victoria), was reported by G. vom Rath,[1] and R. W. E. MacIvor; while a mineral, which appeared to be a mixture of newberyite and struvite, from Quarz Creek (Dawson City, Yukon), was analyzed by G. C. Hoffmann.

A. de Schulten [2] obtained microscopic crystals of **monohydrated magnesium hydrophosphate,** $MgHPO_4.H_2O$, by heating a soln. of magnesium carbonate in an excess of phosphoric acid for some hours in a sealed tube at 225°. A. F. de Fourcroy, A. Riffault, T. Graham, L. Schaffner, and C. G. Reischauer prepared **trihydrated magnesium hydrophosphate,** $MgHPO_4.3H_2O$, in needle-like crystals, by the mixing of a soln. of, say, 2 parts of magnesium sulphate in 32 parts of water, with 3 parts of decahydrated disodium hydrophosphate in 32 parts of water, and allowing the soln. to stand 24 hrs. at a temp. above 36°. H. Rose stated that if very dil. soln. are employed, the normal phosphate is produced. H. Debray made this compound by neutralizing an aq. soln. of phosphoric acid with magnesium carbonate, the precipitated heptahydrate was filtered off. On boiling the filtrate, small crystals of this salt separated from the soln. H. Struve added that only the trihydrate is produced if the boiling soln. of phosphoric acid is treated with magnesium oxide or carbonate, until the liquid has only a feeble acid reaction. J. Stocklasa made the trihydrate by heating dihydrated magnesium tetrahydrophosphate in the solid state or in alcoholic soln. at 100°. B. W. Gerland also made the trihydrate from a soln. of the normal phosphate in sulphurous acid. A. de Schulten mixed a soln. of 16 grms. of heptahydrated magnesium sulphate in 120 c.c. of water with a soln. of 20 grms. of diammonium hydrophosphate, 10 grms. of ammonium sulphate, and 12 grms. of phosphoric acid in 80 c.c. of water, and in 24 hrs. obtained crystals of struvite, $Mg(NH_4)PO_4.6H_2O$, which when left in contact with the mother liquid did not change; but when a more conc. soln. of the magnesium sulphate was employed, a mixture of crystals of struvite and newberyite, $MgHPO_4.3H_2O$, was formed, and when allowed to stand in contact with the mother liquid, the latter increased at the expense of the former.

According to F. K. Cameron and J. M. Bell, when mixtures of phosphoric acid and magnesium oxide are agitated for two months, the clear soln. contains, per litre, at 25°,

MgO .	0·207	2·23	26·09	75·5	122·6	146	160	87·1	70·6
P_2O_5 .	0·486	7·35	93·09	281·8	498	623	700	779·6	835·1
Sp. gr. .	—	1·006	1·109	1·285	1·470	1·595	—	1·626	1·654
Solid phases				$MgHPO_4.3H_2O$				$Mg(H_2PO_4).nH_2O$	

The graph of the results is shown in Fig. 29 in connection with magnesium dihydrophosphate.

H. Debray claimed to have made crystals of **enneahemihydrated magnesium hydrophosphate,** $MgHPO_4.4\frac{1}{2}H_2O$, by allowing magnesium carbonate to stand for some days in contact with phosphoric acid. A. F. de Fourcroy, T. Graham, C. G. Reischauer, A. Riffault, and L. Schaffner prepared **heptahydrated magnesium hydrophosphate,** $MgHPO_4.7H_2O$, by the process employed for the trihydrate, but keeping the mixture at a temp. below 36°. T. Bergmann probably also made this salt by evaporating a soln. of magnesium oxide in phosphoric acid, and J. J. Berzelius by evaporating a mixed soln. of magnesium acetate and phosphoric acid. L. Chevron and A. Droixhe prepared the heptahydrate by digesting a soln. of potassium dihydrophosphate with magnesium oxide or hydroxide, and allowing the filtered soln. to stand at ordinary temp. According to J. Percy,

the amorphous precipitate of the heptahydrate becomes crystalline when exposed to the action of carbon dioxide.

The **crystals** of the monohydrate were stated by A. de Schulten to behave in polarized light as if they belonged to the rhombic system, but that they are really monoclinic twinned complexes, and resemble the trihydrated pyrophosphate. The trihydrate forms acicular crystals or rhombic six-sided plates, which, in the natural state, according to A. Schmidt, belong to the rhombic system, and have the axial ratios $a : b : c = 0{\cdot}9548 : 1 : 0{\cdot}9360$. The heptahydrate also forms small six-sided columnar or acicular crystals which, according to K. Haushofer, are monoclinic prisms with axial ratios $a : b : c = 0{\cdot}4451 : 1 : 0{\cdot}2177$, and $\beta = 94° 18'$. A. de Schulten found that the **specific gravity** of the monohydrate is 2·326 at 15°; the natural trihydrate, according to A. Schmidt, has a sp. gr. 2·10, and **hardness** 3.

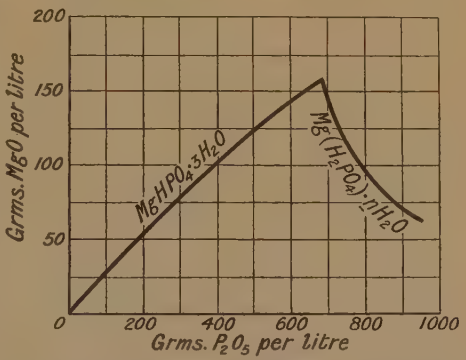

FIG. 29.—Equilibrium between Magnesium Oxide and Phosphoric Acid in Aqueous Solutions at 25°.

A. de Schulten stated that the monohydrate loses no water when heated to 100°. According to H. Struve, the trihydrate loses water when heated above 100°, while T. Graham found that the trihydrate loses its water of crystallization at 170°, and at a higher temp. it forms the pyrophosphate. T. Graham, and L. Schaffner found that the heptahydrate rapidly effloresces in dry air, and loses three-sevenths of its water of crystallization at 100°, and at a higher temp. the pyrophosphate is formed; according to A. F. de Fourcroy, the salt melts to a transparent glass when heated to a still higher temp. H. Struve found that the heptahydrate, according to the mode of preparation, loses 4 to 4·5 mols of water at 100°. C. G. Reischauer stated that when the heptahydrate, dried over sulphuric acid, is heated in a closed vessel, it passes into the trihydrate, and appears to become moist; but the undried heptahydrate loses 5·5 mols over sulphuric acid, and the product does not absorb quite enough water to produce the trihydrate when it is exposed to moist air. According to M. Berthelot, the **heat of formation** of crystalline $MgHPO_4$ from its elements is 413·6 Cals., and from magnesium sulphate and disodium hydrogen phosphate is —0·79 Cal. when the amorphous salt is produced, and when this becomes crystalline, 1·80 Cals. are set free, so that the total heat of formation of the crystalline salt is 1·01 Cals. The **heat of neutralization** of phosphoric acid with magnesium hydroxide to form $MgHPO_4$ is 25·30 or 27·10 Cals. depending on whether the amorphous or crystalline salt is produced. A. Schmidt found newberyite has the **index of refraction** $\mu_\beta = 1{\cdot}5196$ for Na-light, and the **double refraction** is positive. P. Bary stated that the heptahydrate does not fluoresce either in **X-rays** or in **Becquerel's rays.**

According to H. Struve, 100 parts of water dissolve 0·025 part of the trihydrate; and F. Graham found that after several days' digestion 100 parts of cold water dissolve 0·3106 part of the heptahydrate; the soln. becomes turbid at 49°, and milky at 100° in consequence of the separation of the unchanged salt; a boiling sat. soln. contains 0·2008 part of the salt in 100 parts of water. Any salt which has been deposited from the soln. by raising the temp., is re-deposited on cooling. L. Schaffner found that digestion with boiling water frequently renewed converts the hydrophosphate into the normal salt (*q.v.*), and the soln. contains the dihydrophosphate, $Mg(H_2PO_4)_2$. H. Debray also heated the hydrophosphate with water in a sealed tube at 120°, and obtained the normal salt. A. Riffault, however, said that boiling water decomposes the hydrophosphate into a soluble acid salt and an

insoluble basic salt. According to T. Graham, magnesium hydrophosphate is much more soluble in water containing a trace of one of the **acids**—phosphoric, sulphuric, hydrochloric, nitric, oxalic, or acetic acid—and the soln. thus obtained does not become turbid when boiled. *Vide supra* for B. W. Gerland's observations on the solubility of magnesium hydrophosphate in **sulphurous acid.** C. A. Lesueur found that precipitated hydrophosphate absorbs **ammonia,** and is transformed into ammonium magnesium phosphate ; A. Pavesi and E. Rotondi said that the absorption is incomplete ; and H. Lutschak, that the precipitate dried at 100° does not absorb ammonia. According to A. Joannis, when magnesium hydrophosphate is left for three days in contact with liquid ammonia, only an insignificant amount is absorbed.

J. Stoklasa [3] prepared **dihydrated magnesium dihydrophosphate,** $Mg(H_2PO_4)_2.2H_2O$, by digesting on a water-bath magnesium oxide in a conc. soln. of phosphoric acid of sp. gr. 1·4, so that the product contains from 5 to 7 per cent. of free phosphoric acid ; the soln. is evaporated until crystallization begins, then cooled, and the crystals washed with ether, pressed between filter-paper, again washed with ether until no more phosphoric acid is removed, and then dried in a stream of air. F. K. Cameron and J. M. Bell treated trihydrated magnesium hydrophosphate with soln. of phosphoric acid of varying conc. The stable solid in contact with the more dil. soln. is $MgHPO_4.3H_2O$, but with conc. soln. containing over 700 grms. P_2O_5 per litre, the solid phase is $Mg(H_2PO_4)_2.nH_2O$. The observed results are indicated in connection with magnesium hydrophosphate. For soln. in contact with magnesium hypophosphate the proportion of magnesium oxide in soln. increases regularly with increased conc. of phosphoric acid, whilst for those in equilibrium with the latter salt, the conc. of magnesium oxide diminishes with increasing phosphoric acid conc. Some evidence has been obtained that a magnesium phosphate more basic than the diphosphate exists at 25° in contact with very dil. soln. of phosphoric acid.

The radial aggregates of the crystals are not particularly hygroscopic, they absorb about one per cent. of water from the air of a room, and from an atm. sat. with water-vapour, in 24 hrs. 6–7 per cent. of water which is given off again in dry air. When dehydrated at 100°–170°, J. Stoklasa found that anhydrous **magnesium dihydrophosphate,** $Mg(H_2PO_4)_2$, is formed as a white opaque crystalline mass, which remains unchanged in air, and is non-hygroscopic. At 175°, the dihydrophosphate decomposes : $4Mg(H_2PO_4)_2=3Mg(H_2PO_4)_2+MgH_2P_2O_7+H_2O$; at 184°, $4Mg(H_2PO_4)_2=2Mg(H_2PO_4)_2+2MgH_2P_2O_7+2H_2O$; at 196°, $4Mg(H_2PO_4)_2=Mg(H_2PO_4)_2+3MgH_2P_2O_7+3H_2O$; and at 205°, $4Mg(H_2PO_4)_2=4MgH_2P_2O_7+4H_2O$—*vide infra* for the dihydropyrophosphate—100 c.c. of water dissolve 20 grms. of anhydrous dihydrophosphate, without decomposition, and thus the behaviour is different from the corresponding calcium salt ; nor does an aq. soln. of magnesium dihydrophosphate decompose at 60° ; but with alcohol the salt is decomposed : $Mg(H_2PO_4)_2.2H_2O+H_2O=MgHPO_4.3H_2O+H_3PO_4$; the reaction progresses rapidly at 100°, and with a great excess of alcohol is quantitative.

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§ 22. Magnesium Pyrophosphates

When magnesium hydrophosphate or ammonium magnesium phosphate is heated, normal **magnesium pyrophosphate,** $Mg_2P_2O_7$, remains as a transparent glass. Z. Karaoglanoff and P. Dimitroff [1] found that if the ammonium magnesium phosphate is precipitated slowly while boiling, the conversion to pyrophosphate by ignition is not attended by incandescence; the converse obtains if the salt is precipitated rapidly at a lower temp. Traces of organic matter are also necessary for the incandescent effect. According to H. Rose, an aq. soln. of pyrophosphoric acid gives a precipitate of **trihydrated magnesium pyrophosphate,** $Mg_2P_2O_7.3H_2O$—according to the analyses of the crystalline and amorphous salts by A. Schwarzenberg—when added to a soln. of magnesium sulphate in the presence of ammonium chloride and ammonia; this salt is soluble in much water; while normal sodium pyrophosphate gives a precipitate with magnesium sulphate which is soluble in an excess of both agents; when the mixture is boiled, a precipitate again forms which does not redissolve on cooling. G. F. Wach stated that sodium dihydropyrophosphate gives no precipitate with magnesium sulphate until further addition of ammonium carbonate, and the precipitate which is then formed contains but a trace of ammonia, and is dissolved by an excess of either magnesium sulphate or the sodium dihydropyrophosphate. According to A. Schwarzenberg, when a soln. of magnesium oxide in one of sodium dihydropyrophosphate is heated, gelatinous magnesium pyrophosphate, resembling aluminium hydroxide, separates out; when this is dissolved in sulphurous acid, and boiled, it appears as a crystalline powder.

O. Andersen found that colourless glass-like tabular **crystals** were readily obtained by cooling fused magnesium pyrophosphate; the monoclinic crystals have the axial ratios $a:b:c=0{\cdot}7947:1:1{\cdot}0880$, and $\beta=75°\ 49'$. By twinning, the crystals often approximate to the rhombic form. Z. Karaoglanoff and P. Dimitroff said that if the pyrophosphate is produced with incandescence by the ignition of ammonium magnesium phosphate, it is hard, grey to black, and lava-like; if not produced with incandescence, it is an amorphous powder, loose in texture. F. W. Clarke found the **specific gravity** of the anhydrous, probably amorphous, normal pyrophosphate is 2·559 at 18°, and 2·598 at 22°; H. G. F. Schröder gave 2·20. O. Andersen showed that the crystals have a sp. gr. 3·058 at 25°/4°. The **hardness** is a little below 4. A. Schwarzenberg noted that both the amorphous and crystalline salt lose all the water of crystallization at 100°. O. Andersen measured the **indices of refraction** for Na-light, and found $\mu_\alpha=1{\cdot}615\pm0{\cdot}003$; $\mu_\beta=1{\cdot}604\pm0{\cdot}003$; $\mu_\gamma=1{\cdot}602\pm0{\cdot}003$; and the maximum positive **double refraction** is $\alpha-\gamma=0{\cdot}013\pm0{\cdot}005$. P. Bary stated that the salt does not fluoresce when exposed to the **X-rays,** or to **Becquerel's rays.**

H. Struve found that when heated white hot in a stream of **hydrogen,** magnesium pyrophosphate is reduced developing phosphorus and phosphine. C. R. Fresenius stated that the salt is easily soluble in **hydrochloric acid;** while T. Graham said that it is dissolved with difficulty by that acid. According to R. Weber, and C. R. Fresenius, magnesium pyrophosphate is not completely precipitated as ammonium magnesium phosphate, when the acid soln. is neutralized with ammonia. R. Weber stated that when boiled with **sulphuric acid,** it is converted into the normal salt, while H. Pellet stated that it is transformed into *magnesium pyrosulphophosphate.* Magnesium pyrophosphate is readily dissolved in nitric acid, and the soln. behaves towards ammonia like the soln. in hydrochloric acid. According to D. Campbell,

the soln. in **nitric acid** furnishes crystals of magnesium nitrate when evaporated to a syrupy consistence by standing over conc. sulphuric acid; and, according to E. Luck, if the soln. is evaporated to complete dryness, a white gum-like mass remains which has an acid reaction, and which is regarded by D. Campbell, and E. Luck, as a magnesium nitritophosphate, $2MgO.H_2O.P_2O_5.NO_2$. H. Rose found that the pyrophosphate is completely converted into the normal phosphate by fusion with **sodium carbonate.**

According to J. Stoklasa, when magnesium dihydrophosphate is heated to 205°, **magnesium dihydropyrophosphate,** $MgH_2P_2O_7$, is formed; and he also found when $Mg(H_2PO_4)_2.2H_2O$ is heated for 2 hrs. at

	210°	220°	240°	260°	280°	295°	303°
Per cent. loss . .	22·4	22·42	23·28	23·64	23·66	26·99	28·50

The calculated loss for the formation of $MgH_2P_2O_7$ is 21·26 per cent. and for $Mg(PO_3)_2$, 28·35 per cent.

A. Beer, and H. Ludwig prepared **sodium magnesium pyrophosphate** by gradually adding magnesium chloride to a boiling soln. of sodium pyrophosphate. The amorphous precipitate is washed with water containing ammonia. The precipitate is soluble in water, and readily soluble in hydrochloric or nitric acid; J. F. Persoz, and A. Schwarzenberg obtained a similar precipitate which dissolved in an excess of the sodium pyrophosphate furnishing a liquid which soon became turbid and congealed to a gelatinous solid on standing. L. Ouvrard obtained crystals of $Na_2MgP_2O_7$ by slowly cooling a soln. of magnesium oxide, chloride, or phosphate in fused sodium orthophosphate or pyrophosphate, and extracting the mass with water. The dendritic crystals probably belong to the cubic system; their sp. gr. is 2·2 at 20°. K. A. Wallroth obtained transparent prisms with the composition $Mg_{10}Na_{16}(P_2O_7)_9$ by dissolving the metallic oxide in microcosmic salt heated to a bright red heat; the glass so formed is maintained in a state of fusion until the crystals have separated out. On cooling, the mass is digested with water, and then with dil. hydrochloric acid. L. Ouvrard obtained the same compound. The transparent prisms are probably monoclinic; their sp. gr. is 2·7 at 20°; they fuse to a transparent glass; and are readily soluble in acids. M. Berthelot and G. André prepared the triple salt **ammonium sodium magnesium pyrophosphate,** $(NH_4)_3NaMg_6(P_2O_7)_4$, by precipitation from a soln. of normal sodium pyrophosphate with magnesia mixture; the precipitate is dissolved by adding a great excess of ammonium chloride, and the soln. acidified with acetic acid. When boiled for a long time, the compound in question separates out. It is insoluble in, and undecomposed by water; but a prolonged washing with acetic acid extracts magnesium. No ammonia is lost at 110°. There is doubt about the individuality of these products.

T. Fleitmann and W. Henneberg [2] prepared **magnesium tetraphosphate,** $3MgO.2P_2O_5$, by precipitation from a soln. of magnesium sulphate by adding the sodium salt; or by fusing together the salts and leaching the product with water. The white insoluble crystalline powder becomes insoluble in acids when heated to a high enough temp. M. Stange prepared **sodium magnesium triphosphate,** $Na_3MgP_3O_{10}.13H_2O$, by adding a soln. of magnesium chloride to one of sodium triphosphate until a permanent precipitate begins to form; this is quickly redissolved by the addition of sufficient triphosphate, and the salt then at once commences to separate. It crystallizes in very slender needles, is decomposed by exposure to air, losing water of crystallization, and, when heated, intumesces like borax, and melts at a red heat to a clear glass easily soluble in acids.

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§ 23. Magnesium Metaphosphates

According to R. Maddrell,[1] **magnesium metaphosphate** is formed by dissolving magnesium carbonate in an excess of dil. phosphoric acid, evaporating the soln. to dryness, and heating the residue to 316°; or, according to J. Stoklasa, by heating magnesium dihydrophosphate to 305°. It appears as a glassy mass, which, according to T. Fleitmann, is not changed by digestion for a day with soln. of alkali carbonate or phosphate, and it is therefore not clear to which particular metaphosphate this product belongs.

A. Glatzel made anhydrous **magnesium dimetaphosphate,** MgP_2O_6, by evaporating a soln. of magnesium carbonate in aq. phosphoric acid, with about one per cent. in excess, first on a water-bath, then on a sand-bath, and finally at 400°. The pulverized mass was washed with cold water slightly acidified with nitric acid. The resulting crystalline powder is strongly attacked by sulphuric, nitric, or hydrochloric acid. T. Fleitmann prepared **hydrated magnesium dimetaphosphate,** $MgP_2O_6.nH_2O$—where n=4 according to A. Glatzel, and 4·5 according to T. Fleitmann—by mixing conc. soln. of his ammonium dimetaphosphate, $(NH_4)_2P_2O_6$, with an excess of magnesium chloride, and allowing the mixture to stand for some time. The resulting crystals do not dissolve in water, and are not decomposed by acids; but conc. sulphuric acid was found by A. Glatzel to dissolve readily the salt, forming, when boiled, normal phosphoric acid. T. Fleitmann found that the calcined salt is not changed by soln. of alkali carbonates or phosphates. At 100°, the hydrated salt loses about 2 per cent. of water, and the remainder on calcination. T. Fleitmann stated that some phosphoric oxide is lost at the same time, but A. Glatzel said that this is wrong.

A. Glatzel prepared tetrahydrated **sodium magnesium dimetaphosphate,** $Na_2Mg(P_2O_6)_2.4H_2O$, as a crystalline powder by mixing conc. soln. of sodium dimetaphosphate and magnesium chloride. The complex salt loses its water of crystallization completely at a dull red heat, sinters at a higher temp., and passes without melting into polymerized phosphoric acid. Before calcination, the salt is readily soluble in sulphuric, hydrochloric, and nitric acids, but after conc., it is soluble only in conc. sulphuric acid. 100 c.c. of water dissolve 4 grms. of the salt. A. Glatzel prepared the corresponding tetrahydrated **potassium magnesium dimetaphosphate,** $K_2Mg(P_2O_6)_2.4H_2O$, in a manner similar to that employed for the sodium salt. It loses its water of crystallization at 150°, and after heating to redness, it is not affected by soln. of alkali carbonates. It does not fuse at a bright red heat. 100 parts of water dissolve 9·84 parts of salt. The salt is readily decomposed by acids—particularly boiling sulphuric acid—forming phosphoric acid. According to L. Ouvrard, when magnesia is dissolved in potassium metaphosphate, the sole product is the compound $K_2Mg_2(P_2O_6)_3$, which crystallizes in large, monoclinic prisms, very soluble in dil. acids; sp. gr. at 20°=2·4. It is analogous to the double magnesium sodium phosphate obtained by T. Fleitmann and W. Henneberg in the wet way.

T. Fleitmann prepared hydrated **ammonium magnesium dimetaphosphate,** $(NH_4)_2Mg(P_2O_6)_2.nH_2O$, by mixing soln. of ammonium dimetaphosphate and magnesium chloride. A. Glatzel found the crystals lose all their water at 150°. T. Fleitmann said that the hydrate contains 6 mols of water, and effloresces in air; *au contraire*, A. Glatzel said the crystals contain 4 mols of water, and do not lose weight even when confined over conc. sulphuric acid. The latter also stated that the crystals lose ammonia at a dull red heat, and at a bright red heat, phosphoric oxide; at a still higher temp. the product melts and forms magnesium tetrametaphosphate. The double salt is easily attacked by acids.

According to G. F. Wach, when a soln. of recently ignited metaphosphoric acid in aq. ammonia is added to one of magnesium sulphate, the precipitate first formed is redissolved so long as an excess of the latter is present, but when the former is in excess, the precipitate remains undissolved. Alcohol precipitates the portion still remaining in soln. An excess of magnesium chloride, nitrate, or acetate gives the same precipitate, but does not dissolve it so readily. The precipitate forms feathery flakes which unite to form a stringy viscid mass which, after being washed with water and dried, becomes transparent and brittle like glass. When the product is heated in a glass tube, it swells up, forming an opaque spongy mass with the evolution of water at first, and afterwards ammonia. The residue does not fuse at the temp. at which glass softens; it dissolves in water with difficulty to form a soln. with an acid reaction, but is itself slightly soluble in acids. The undecomposed double salt dissolves somewhat freely in cold water, but is precipitated on the addition of alcohol. The cold soln. has an acid reaction towards litmus, and deposits the salt as a viscid mass, when heated, but re-dissolves it on cooling. In boiling water, the salt swells to an opaque frothy mass, without any considerable proportion passing into soln. The analyses of the double salt do not correspond with a definite magnesium ammonium meta- or pyro-phosphate.

G. Tammann has argued that the so-called magnesium dimetaphosphate is really **hydrated magnesium trimetaphosphate,** $Mg_3(P_3O_9)_2.14H_2O$. C. G. Lindbom prepared dodeca- and pentadeca-hydrated trimetaphosphates by crystallization from a mixed soln. of two parts of hexahydrated magnesium chloride, and one part of sodium trimetaphosphate, at 20° to 30°—either the one or the other hydrate appears. When the crystals are dried on the water-bath they retain about 10·5 mols of water, which is all lost at a red heat, without melting. The residue is insoluble in boiling hydrochloric acid. The salt is sparingly soluble in water, and the soln. is neutral. When the aq. soln. is treated with aq. ammonia and normal sodium phosphate, the salt is precipitated. T. Fleitmann and W. Henneberg, and C. G. Lindbom have prepared sodium magnesium trimetaphosphate, $Na_4Mg(P_3O_9)_2.5H_2O$. The latter evaporated a mixed soln. of hexahydrated magnesium chloride with about four times its weight of sodium trimetaphosphate at 20° to 30°, and obtained a crystalline crust, which was washed with a little water. Over conc. sulphuric acid, about one-tenth of the water of crystallization was removed, and all was expelled at a high temp. The product melts at a red heat, forming an opaque white mass which deliquesces in air, and furnishes a soln. of sodium hexametaphosphate when treated with water, and magnesium metaphosphate remains. The double salt dissolves slowly in water, the soln. is neutral, and is not precipitated by sodium carbonate or disodium hydrophosphate unless ammonia has been previously added.

According to A. Glatzel, when magnesium dimetaphosphate is melted, and slowly cooled, **magnesium tetrametaphosphate,** $Mg_2P_4O_{12}$, is formed. The salt crystallizes in stellate aggregates. It is insoluble in water, and is attacked by hydrochloric acid, still more by nitric acid, and quite vigorously by conc. sulphuric acid. When digested for a day with a soln. of alkali carbonate, the alkali tetrametaphosphate is formed. When a dil. soln. of ammonium tetrametaphosphate is treated with an excess of magnesium chloride, small white crystals of **decahydrated magnesium tetrametaphosphate,** $Mg_2P_4O_{12}.10H_2O$, are formed. 100 parts of water dissolve 1·43 parts of the salt. The hydrate is decomposed by acids, particularly conc. sulphuric acid. When calcined, the whole of the water is driven off, and the molten mass is glassy when rapidly cooled. According to H. Rose, an aq. soln. of hexametaphosphoric acid gives a precipitate of **magnesium hexametaphosphate,** when

added to a soln. of magnesium and ammonium chlorides. The precipitate is soluble in much water. T. Graham found that a gum-like precipitate is obtained when sodium hexametaphosphate is added to a soln. of magnesium acetate, but not to one of magnesium sulphate. H. Rose obtained no precipitate by adding aq. ammonia to a soln. of magnesium sulphate mixed with a sufficient quantity of sodium hexametaphosphate.

W. Gregory accidentally discovered what G. Tammann considers to be **sodium magnesium octometaphosphate,** $Na_2Mg_3P_8O_{24}$, in the preparation of phosphoric acid. In the extraction from bones by J. von Liebig's process, there is first a separation of magnesium metaphosphate, $Mg(PO_3)_2$, and then by repeated dilution and heating, the double octophosphate appears, which can be separated from the excess of phosphoric acid by treatment with cold water. G. Tammann obtained the double salt by melting a mol of a magnesium compound with a mol of tetrahydrated ammonium sodium hydrophosphate, and stirring the mass as it cools. The crystals are said to be rhombic dodecahedra, which, when dried at 100°, are free from water. According to W. Gregory, and R. Maddrell, the salt is insoluble in water or aq. phosphoric acid, soluble in conc. sulphuric acid, and slightly soluble in hydrochloric acid and aqua regia. G. Tammann said that the salt is insoluble in the two last-named menstrua ; and that alkali sulphides have scarcely any action on the salt.

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CHAPTER XXX

ZINC AND CADMIUM

§ 1. The History of Zinc and Cadmium

Gold and silver excepted, there is no metal which has had formerly so many and so wonderful names as zinc.—J. BECKMANN.

The history of zinc furnishes a remarkable example how slowly progress is made when observations are not interpreted by the scientific method, and when the fundamental laws concealed in a phenomenon have not been recognized.—F. X. M. ZIPPE.

THE mode of preparing *orichalcum* or *brass* from copper was known over 2000 years before the metal zinc was discovered, and it required a good many years' more observation before the alloying of the two metals, zinc and copper, was recognized as the essential process involved in the manufacture of brass. It is not surprising, said J. Beckmann,[1] that zinc should have remained so long unknown, for it had never been found in the metallic state. Its ores are often and in a great degree mixed with foreign ingredients; and when they are melted, the zinc sublimes in a metallic form, and is found adhering to the cool sides in the upper part of the furnace; but a particular apparatus is necessary, else the reduced metal partly volatilizes, and is partly oxidized, by which means it appears like an earth, and exhibits to the eye no traces of metal.

The term *brass* is mentioned several times by the biblical writers—nearly 4000 years B.C., for instance, we are told in *Genesis* (**4**. 32), that Tubalcain was a worker in brass and iron; and the brass or bronze looking-glasses of women are mentioned in *Exodus* (**38**. 8). There are also frequent references to brass or bronze in the early writings of Homer, about 1000 B.C., and of Hesiod, about 700 B.C. So far as we can gather, the early writers confused copper, brass, and bronze because the same term was employed for any or all these metals. The word rendered brass should be translated bronze. It is known that it was customary in very early times for women to wear a bronze mirror as an article of dress; M. H. Klaproth has analyzed one such, and found: copper, 62; tin, 32; and lead, 6 per cent.

In the work ἐν Θαυμασίοις—on marvels—wrongly attributed to Aristotle about 320 B.C., but more probably written about the middle of the third century, it is said that bronze without tin was made at Mossynœcia, near the Black Sea, by melting copper with a peculiar earth which was found in the neighbourhood. In the first century of our era, Dioscorides, in his *De materia medica*, and Pliny, in his *Naturalis historia* (**34**. 2), called the earth καδμεῖα or *cadmia*, and the latter, probably both, used the term for the flue-dust which collects in smelting furnaces. C. Salmasius said that Dioscorides meant a native earth rich in zinc; and J. Beckmann, that he meant furnace-calamine. The name is perhaps derived from Cadmos, the son of Agenor and Telephasse, who brought the κάδμου τέχνη from Phœnicia to Greece, and καδμεῖα may be analogous with Theban earth. According to E. O. von Lippmann,[2] the metal zinc is not mentioned in the Ebers' papyrus, nor was it known as a metal to Aristotle, Dioscorides, or Pliny. The metal is not mentioned by Marco Polo in his travels in Persia at the end of the thirteenth century, although he describes *tutia* or *totia*. The Arabians who translated the Greek writers speak of the preparation of brass, but they have nothing to say about the metal zinc.

It is probable that the alloy known as orichalcum or brass, tombac, pinchbeck,

etc., was first discovered by smelting cupriferous zinc ores which yielded not copper but brass. Mines that contained ores, from which the gold-coloured metal was produced, were held in the highest esteem, and the early brasses seem to have been obtained by the smelting of such ores from mines in Laurium (near Athens), Sardinia, and Cyprus.[3] In course of time, it was observed, possibly by accident, that an earth, which was probably calamine, when added to molten copper gave it a yellow colour; and this as a method of preparation was found to be more convenient than procuring the brass from zinciferous copper ores. This is the method to which the pseudo-Aristotle above refers. According to E. von Bibra,[4] the Greeks were not acquainted with the manufacture of brass, but that alloy was made about the time of Augustus, near the beginning of the Christian era, by heating copper with certain earths—presumably containing zinc, *e.g.* calamine, galmei, or tutty—mixed with carbon. Brass was thus known to the Romans; and about the eleventh century, the process of manufacture was described by the monk Theophilus.[5] As the zinc was reduced, it alloyed with the copper by cementation, forming the golden-yellow colour characteristic of a low-zinc brass. It is remarkable that the same word *cadmia* should have been employed for both the zinciferous ore and the flue-dust—an impure zinc oxide—found in furnaces smelting zinciferous ores. According to J. Beckmann, the term *tutia*, employed by Avicenna in the eleventh century, seems to have been used in a similar manner. A work attributed to Zosimus of Panopolia stated that brass is made by melting Cyprian copper with *tutia*. In spite of this, the furnace-calamine, which collected about the furnaces at Rammelsberg, was rejected as useless until the middle of the sixteenth century, when E. Ebener, about 1548, discovered that it could be employed in making brass.

The alloy was termed orichalcum by the Romans, who obtained the word from the Greeks' ὀρείχαλκος=ὄρος, a mountain, and χαλκός, copper or bronze. The term *aurichalcum* is a mis-spelling [6] due to the resemblance which *orichalcum* bears to *aurum* (gold); and the term aurichalcum reappears, still more corrupted, in the French *archal*. It has been suggested that the German term *Messing* for brass is a corrupt form of Mossynœcia [7]—*vide supra*. Both words, orichalcum and aurichalcum, were used for brass about the beginning of the Christian era, but they were probably also employed in some cases for bronze. Attempts have been made to derive the term *zinc* from the Persian *tscheng*, or the newer Persian *seng*.

According to Cicero,[8] who wrote near the beginning of our era, Roman coins made from orichalcum were undistinguishable from gold, and he raised the ethical question whether an honest man should acquaint a person who was really selling *aurum* but thought he was selling *orichalcum*, or should he buy for a penny what was worth a thousand times as much? The only metal which the Romans could have so mistaken for gold is the alloy of copper and zinc now called brass. Several brass coins of the Roman period have been analyzed by J. Percy,[9] W. Gowland, J. A. Phillips, F. Göbel, H. Garland, etc. A selection of these analyses by W. Gowland is indicated in Table I. Traces of nickel, antimony, and arsenic were reported

Table I.—Analyses of Ancient Brasses.

Brass.	Date.	Cu	Sn	Zn	Pb	Fe
Augustus coin	30 B.C. to 14 A.D.	87·05	0·72	11·80	tr.	0·43
Tiberius coin	41 A.D.	72·20	—	27·70	—	—
Nero coin	54 A.D. to 68 A.D.	77·44	0·30	21·50	tr.	0·32
Vespasian coin	71 A.D.	81·97	—	18·68	0·14	0·12
Trajan coin	98 A.D. to 107 A.D.	77·59	0·39	20·70	—	0·27
Sabina coin	100 A.D. to 137 A.D.	82·35	0·43	16·84	tr.	0·38
Memorial brass (England)	1456	67·54	1·16	24·16	7·14	—
Memorial brass (England)	1504	64·50	3·00	29·50	3·50	—
Statue (Munich)	1600	76·90	0·64	19·69	2·68	0·17

in the first and sixth alloys, and 0·20 per cent. of antimony and 0·24 per cent. of nickel in the third, and 0·10 per cent. of nickel in the last one. According to F. Göbel, zinc is found only in alloys of Roman origin. The bronze objects derived from the Greeks and their colonies in Italy, Egypt, Asia, etc., invariably consist of copper and tin, with or without lead.

Scholars have not been able to find in the works of any other classical author one single statement which would support the view that the Greeks or Romans were acquainted with the element zinc; but there are some reputed finds of the metal among ancient remains. According to G. F. C. Fuchs,[10] the oldest piece of zinc extant is an idol found in a prehistoric Dacian settlement at Dordosch, Transylvania. It contained: zinc, 87·52; lead, 11·41; and iron, 1·07 per cent. According to P. C. Grignon, in 1772, a small metal bar of zinc was found in the ruins of an old Roman town at Champagne. He said that the bar had been worked to some extent, and added that in the neighbourhood of the town, there was an iron mine containing a great deal of zinc. A zinc relic has also been reported from the ruins of Pompeii (destroyed 79 A.D.); and M. Salzmann found in the ruins of Camiros (Isle of Rhodes), destroyed 500 B.C., a bracelet of silver inlaid with zinc. *Voici deux faits positifs*, said R. Jagnaux, *qui prouvent indubitablement que les anciens ont su extraire le zinc de ses minerais;* but J. Beckmann said that the first case had been examined only in a superficial manner; and there is nothing to show what kind of a metal or alloy P. C. Grignon considered to be zinc. K. B. Hofmann[11] questions the Pompeian find because a search for the fountain in the museum at Naples has not been successful. There is a hint in Strabo's *Geographia* (**13.** i, 56), written about 20 A.D., of a kind of mock-silver—ψευδάργυρον, or *pseudo-argyrum*—which furnished *orichalcum* when heated with copper. The ancient geographer said:

> There is a stone near Andeira which becomes iron when it is burnt, and afterwards, when it is melted in a furnace with a certain earth, it drops mock-silver, which with the addition of copper, produces what is called . . . orichalcum. Mock-silver is also found in the neighbourhood of Tenolus.

The term *pseudoargyrum* or mock-silver must here have been intended to represent a metal with a certain resemblance to silver, but the only metals then known to have the colour of silver were mercury, lead, and tin; and the first two of these would not communicate to copper the properties ascribed to *orichalcum* nor does the description fit well with tin. It has therefore been conjectured that metallic zinc was known in the first century of our era. It is, however, unlikely that zinc would collect in drops like Strabo's *pseudoargyrum* unless it be assumed that the furnace was provided with a distillatory and condensing apparatus. J. Percy, however, does mention that occasionally the vapour of zinc may be accidentally condensed in cracks in the walls of furnaces, and trickle down in drops. M. Gsell assumed that Strabo's *pseudoargyrum* was metallic arsenic; F. X. M. Zippe, arsenical copper; and H. W. Schäfer, an arsenical alloy. In any case, P. Diegart and B. Neumann conclude that the *pseudoargyrum* was not metallic zinc.

According to A. J. C. Geerts,[12] the first Chinese book to mention *ya-yuen* (literally, lead of inferior quality) was called *Tien kong kaī ou*, and it was published at the beginning of the seventeenth century; in that work, it is stated that the metal is mentioned only by the then modern writers, not the older ones. The Chinese encyclopædia *Pen tsao kang mu* appeared in the latter half of the sixteenth century, and it contains no reference to zinc, although it is said to have been compiled from the writings of some 800 authors. Calamine brass, however, is described. W. Hommel found a sample of Chinese zinc dated 1745 contained: zinc, 98·99; iron, 0·675; and antimony, 0·245 per cent., and no copper, nickel, silver, lead, or arsenic was present. B. G. Sage has written an account of the early use of zinc money in China.

The Hindu work *Rasarnava*, which appeared between the twelfth and the fourteenth centuries, mentions an essence of the appearance of tin which is obtained by

heating *rasaka* (calamine) with certain organic substances in a covered crucible; and the fourteenth-century book *Rasaratnassamuchchaya* describes an apparatus for obtaining the essence of calamine by distillation—Fig. 1. The essence was not at first classed as a metal, but, according to P. C. Ray, in 1374, K. Madanapala called it *jasada*, and included it among the metals. The Hindus obtained but small quantities of zinc. The technical production and uses of this metal were first described in the Chinese book *Tien kong kaï ou* of 1637. The Chinese encyclopædia *Wa kan sai dzu ye* of 1713, is said to refer to lead as *ya-yuen* and *totan*—from the Sanscrit *tuttham*, and the Persian *tutia*. Calamine is designated in Sanscrit *rasaka*, *kharpara*, and *tutthia*, and the last, when translated into Persian and Arabian, became *tutia*, so that zinc was called *ruh-i-tutia*, literally, the spirit of tutia. In Persia, *white tutia* was zinc sulphate; *blue tutia*, copper sulphate; and *green tutia*, ferrous sulphate. Just as in the sixteenth and seventeenth centuries, the term *counterfey* was applied to all kinds of metals and alloys—zinc, pewter, bismuth, antimonial lead, arsenical copper, etc.—so were the terms for zinc applied to all sorts of metals and alloys. Antimony, or antimonial lead, but not zinc, was described as *kharsini* by Kazwini, the Persian Pliny, in his *Cosmographia*, 1200 A.D. This subject has been discussed by A. I. S. de Sacy. From this it would appear that the art of zinc smelting originated in India, and was carried to China, where zinc was produced on a large scale until the middle of the eighteenth century. According to T. Bergman, zinc was brought to Europe from the East by the Portuguese a century before it was produced as a commercial article in Europe, excepting perhaps a small amount occasionally obtained as a by-product in the lead furnaces of Goslar.

FIG. 1.—Indian Apparatus for Extracting the Essence of Calamine by Distillation *per descensum*.

The alchemists of the Middle Ages, like the Romans, knew that when copper is heated with certain earths, a white arsenical or yellow zincic alloy is formed; and effects of this kind were mentioned in the thirteenth century by Albertus Magnus, in his *De mineralibus et rebus metallicis*, as having been obtained by using what he called *marchasite aurea*. Hence, his golden marcasite was either arsenical or zinciferous pyrites—probably the former. Albertus Magnus, like Pliny, distinguished between *tutia* (furnace calamine) and *lapis calaminaris*, and stated that the former is an artificial product, the latter a mineral, and added that either of these substances imparts a golden colour to copper. He advised the use of glass-gall to be strewn over the molten metal, otherwise the *tutia* or *lapis calaminaris* will lose its force in the fire.

After Albertus Magnus there is a long interval stretching over three centuries during which little or nothing appears to have been written on the subject, but, added J. Beckmann, it was probably not forgotten by the alchemists:

> On account of the great hopes which it gave the alchemists by its colouring copper, they described it purposely in an obscure manner, and concealed it under other names, so that it has not been recognized in their works.

There is, however, no evidence to show that zinc was recognized in Europe as a metal prior to the beginning of the sixteenth century, when Paracelsus employed the term *zinc* for the first time. In his incomplete tract *Liber mineralium*, published posthumously about 1570, Paracelsus wrote:

> There is another metal, *zinckum*, which is in general unknown to the fraternity. It is a distinct metal of a different origin, although adulterated with many other metals. It can be melted, for it consists of three fluid principles, but it is not malleable. In its colour, it is unlike all others, and does not grow in the same manner; but with its *ultima materia* I am as yet unacquainted, for it is almost as strange in its properties as *argentum vivum*. It admits of no admixture, will not bear the *fabrications* of other metals, but keeps itself entirely to itself.

It may be doubted if Paracelsus understood by the term *zinckum* what is understood to-day, since, in another essay, *On the element water*, he said that *zinckum* is a bastard metal from copper, and that bismuth is a bastard metal from tin. He appears to have used the term *bastard metal* for impure separations—possibly calces—which he elsewhere called the *fæces of the pure metals*.

In the sixteenth and seventeenth centuries there was much confusion as to the meaning of the term zinc, and it appears to have been employed locally by the miners of the Kärnthen district for an earthy ore, and generally, not for the metal, but for a number of different minerals. According to J. Mathesius,[13]

> *Counterfey* is a metal of little value formed by additions and colouring substances, so that it resembles silver, as an image, or anything counterfeited, does its archetype. Thus, copper is coloured by calamine and other mixtures, in such a manner that it appears to be pure gold.

In his *De re metallica* (Basiliæ, 1546), published before Paracelsus' tract, G. Agricola mentioned a white metal which he called *counterfei*, and which was found on the walls of a furnace smelting lead ores at Goslar in the Harz, and was probably recognized before Albertus Magnus' time. G. Agricola referred later to the formation of *zincum* in the furnaces of Silesia, but he does not appear to have correlated counterfei with zincum. This was done by G. E. von Lohneyss in 1690, who said that the metal zinc or counterfey greatly resembles tin, and remarked that the metal "zinc or bismuth" was in great demand by the alchemists. J. H. Pott, quoting from Jungius' *Mineralogia*, stated that towards the end of the sixteenth century the sale of zinc from Harz was prohibited by the ruling prince, who had a passion for alchemy, and who appears to have entertained high hopes of its utility in making gold. G. E. von Lohneyss also gave an account of the method of procuring zinc at Goslar. He said:

> The metal *zinc* or *counterfeht* is formed under the smelting furnaces and in the crevices of the wall where the bricks are not well-plastered. When the wall is scraped, the metal falls down in a trough placed to receive it. . . . The metal is not much valued, and the workmen collect it only when they are promised *Trinkgeld*.

A. Libavius used the Hindu term *caläem* for zinc, and in a letter expressed his regret that he had not been able to procure any of the metal; he seems to have regarded zinc as a peculiar kind of tin which took fire when heated in air. J. R. Glauber knew that the zinc brought from the East could be extracted from galmei, calamine, or tutia; and he said:

> Zinc is a volatile mineral or half-ripe metal when it is extracted from its ores. It turns copper into brass as does *lapis calaminaris*, for indeed, this stone is nothing but infusible zinc, and zinc might be called a fusible *lapis calaminaris* inasmuch as both of them partake of the same nature . . . zinc sublimates itself into the cracks of the furnace whereupon the smelters frequently break it out.

P. M. de Respours [14] used the term zinc in his work: *Sur l'esprit minéral*. About this time zinc seems to have been regarded as a compound of two or three elements.

> Albertus Magnus supposed that iron is an ingredient of zinc; Paracelsus called zinc a spurious son of copper; N. Lemery believed it to be a kind of marcasite similar to bismuth; J. R. Glauber considered it to be immature solar sulphur; W. Homberg regarded it as a mixture of tin and iron; J. Kunckel called it a coagulated mercury; and F. de Lassone, and C. F. Wenzel seem to have considered phosphorus to be an essential constituent of zinc, probably because of the fact, observed by J. F. Henckel, that zinc calx phosphoresces when heated.

T. Bergman, in his dissertation *De mineris zinci* (Upsala, 1779), attributed the slow progress in the recognition of the individuality of zinc to the volatile and combustible nature of the metal. When zinciferous products are smelted with copper, the latter fixes the volatile zinc and produces brass. The first stage in the history of zinc is the recognition that a peculiar metal is fixed by copper when certain earths are smelted with that metal. Thus after nearly 2000 years, J. Kunckel

could say that calamine allows its metal part to pass into copper and form brass, and the same idea was advocated by G. E. Stahl. Even as late as 1735, G. Brandt considered that zinc could not be reduced to metal except in the presence of copper. According to W. Hommel, the name and the discovery of the metal have been erroneously ascribed to Basil Valentine; he attributed the demonstration that zinc is the metal of calamine to W. Homberg in 1695; while J. F. Henckel prepared zinc from calamine by heating it with some inflammable substance (phlogiston), but he concealed the method. A. von Swab (1742), and A. S. Marggraf (1746) proved that calamine could be reduced to the metal and distilled in closed vessels in the absence of copper.

The gradual recognition of zinc (i) as a constituent of calamine brass, and (ii) as a chemical individual by the European chemists, was virtually independent of the fact that the metal was brought to Europe by the East Indian traders under the name *tutenag*, *tutanego*, or *tuteneque*, and sold under the name *spiauter*, *spialter*, or *Indian tin*. Robert Boyle [15] called it *speltrum*; the word was spelt in many different ways about that time, and these differences finally crystallized into *spelter*.

The term *spelter* is commonly used for ordinary commercial ingot zinc, whereas the term *zinc* is applied to the rolled metal. Latterly it is common to employ the term spelter for all grades of metal with up to about 99·8 per cent. of zinc; the grades of higher quality being termed *fine-zinc*. The crude zinc being obtained from the ores by smelting is termed *virgin spelter*, or *primary zinc*. Metal that has been remelted is called *remelted spelter*, or *secondary* spelter. The term *hard spelter* refers to a cheap brand of zinc contaminated with iron, a resultant of the galvanizing process.

Although zinc was well known in Europe towards the end of the seventeenth century, the extraction of zinc from its ores attained no industrial importance until early in the nineteenth century. The manufacturers of calamine brass by the cementation process were opposed to the preparation of brass by fusing copper with zinc because, they averred, it produced a brass of inferior quality. The art of zinc distillation, said G. Borgnet, was almost certainly introduced into Europe from the East in the early part of the eighteenth century. T. Bergman records a tradition that a few years prior to 1740, an Englishman went to China to study the smelting of zinc. According to R. Watson, and W. Pryce, Isaac Lawton was the first in England to establish a practical method for extracting zinc from calamine. About 1740, J. Champion established a works at Bristol for the extraction of zinc by distillation *per descensum*. In this process, a covered crucible, fitted with an exit tube leading from the bottom, was heated with the charge in one of the arches of a glass furnace; one furnace carried about half a dozen crucibles. As soon as zinc vapours began to appear at the mouth of the exit tube at the bottom of the crucible, a long condensing tube was attached. The zinc condensed in the tube and collected in suitable trays. Calamine, an important ore of zinc, had previously been used for making brass in various districts—Surrey (*c.* 1650), Bristol (1702), Cheadle (Staffs.) (1720), and later at Smethwick, Swansea, and Llanelly.

According to L. von Wiese,[16] the Bristol process for the extraction of zinc from its ores was started at Wessola (Pless, Silesia), in 1798, by J. R. Ruhberg. An old glass furnace was utilized for the purpose. The works at Wessola were the beginning of the famous Silesian zinc industry. J. R. Ruhberg found that the Bristol process, distillation *per descensum*, was inefficient, and devised a process involving the use of muffles of large capacity. J. J. D. Dony, also, about 1805, started zinc distillation near Liége in Belgium. In 1809, he patented the *Konstruktion eines Ofens, um Zink aus Galmei zu gewinnen und das dazu angewandte Verfahren*. He used a series of small retorts set in a single furnace. The Belgian zinc industry soon became a formidable rival to the Silesian. B. Dillinger, at Dollach (Carinthia), also started distilling zinc from calamine about 1799, but the industry did not flourish here as it did in Silesia and Belgium. Both in Belgium and Silesia zinc was distilled *per ascensum*, and this process proved more economical than the distillation *per descensum* process. Britain

did not keep pace with the advances made in Upper Silesia, in Rhenish Prussia, and in Belgium. The primitive distillation furnaces remained in England until the middle of the nineteenth century, when Britain's lead in the zinc industry declined. It has been said that the failure of British metallurgists to keep pace in the art which they had introduced into Europe from the East, is one of the strange things in the history of metallurgy. Zinc smelting on a smaller scale was adopted in Austria, Spain, Holland, and in France about the middle of the nineteenth century. The regular manufacture of zinc in the United States was started about 1859 by J. Wharton.[17] There has been no radical change in the metallurgy of zinc since the first Belgian furnaces were built in the early part of the nineteenth century.

The history of the discovery of cadmium is comparatively simple. It is a common companion of zinc. In the autumn of 1817, F. Stromeyer,[18] of Göttingen, noticed that a sample of zinc carbonate from the zinc works at Salzgitter was tinged yellow although free from iron, while zinc carbonate from many other sources is white. He attributed the yellow coloration to the presence of a new element, and found indications of the same element in samples of zinc and zinc oxide from several other places. In May, 1818, K. S. L. Hermann, of Schönebeck, examined a sample of zinc which had been condemned because it gave a yellow precipitate, characteristic of arsenic, when an acid soln. was treated with hydrogen sulphide. He found that the yellow precipitate was not arsenic sulphide, but rather the yellow sulphide of a new element. Shortly afterwards, W. Meissner, of Halle, confirmed K. S. L. Hermann's discovery. C. J. B. Karsten, of Berlin, discovered the presence of the new element in the Silesian zinc ores, and he proposed to call the element *melinum*—from *melinus*, a quince—on account of the quince-like colour of the hydrogen sulphide precipitate; L. W. Gilbert proposed the term *junonium*, in honour of the discovery of the asteroid Juno, in 1804; and J. F. John proposed *klaprothium*, in honour of M. H. Klaproth; but F. Stromeyer's proposal *cadmium*—after *cadmia fornacum*, because the element accumulates in the *flowers of zinc*, which collects as fine-dust in zinc furnaces—was finally accepted. F. Stromeyer's element was thought by some to be identical with an element announced by K. S. L. Hermann, and called *vestium* or *vestalium*, but F. Stromeyer showed that the latter announcement was based on a mal-observation. C. H. Roloff has written on the history of cadmium.

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§ 2. The Occurrence of Zinc and Cadmium

Zinc is a common element; cadmium is comparatively rare. F. W. Clarke[1] estimates that zinc is 200 times as abundant as cadmium. There are reports of the occurrence of small quantities of metallic zinc in the basaltic rocks of Brunswick (Victoria),[2] by L. Becker, and by T. L. Phipson. According to G. H. F. Ulrich, this zinc contains about one per cent. of cadmium. L. Becker also reported the occurrence of zinc, containing some cadmium, on the banks of the Mitta Mitta river, New South Wales. J. Park reported finding zinc near Hape Creek (Thames, N.Z.);

W. D. Marks, in N.E. Alabama; and J. D. Dana, in Shasta Co., California. Zinc is present in small amounts in igneous rocks, and traces are also diffused in many sedimentary rocks. J. D. Robertson[3] found the granite, poryphry, and diabase from Missouri contained 0·00139 to 0·0176 per cent. of zinc—average 0·009. Smaller proportions were present in the adjacent limestones, thus, the Silurian limestone contained 0·00016 to 0·01536 per cent. of zinc, and a trace up to 0·00255 per cent. in the lower carboniferous limestone; S. Calvin and H. F. Bain reported 0·00029 per cent. of zinc in the limestones and *dolomites* of Iowa; and A. M. Finlayson obtained results of the same order of magnitude for British rocks and more abundantly in the granites than in the limestones. H. Traube found 1·06 to 1·38 per cent. of zinc carbonate in the *aragonite* of Tarnowitz; and W. Biltz and E. Marcus found zinc and cadmium in the Mermian limestone of Coburg. L. Dieulafait tested hundreds of rocks and always found zinc to be present. F. W. Clarke and G. Steiger found the averages from hundreds of samples:

	Oceanic red clay.	Ferruginous oceanic clays.	Mississippi silt.	American igneous rocks.	Average.
NiO_2 . . .	0·0320	0·0630	0·0170	0·00655	0·0296
As_2O_5 . . .	0·0010	tr.	0·0004	0·00074	0·0050
PbO . . .	0·0073	0·0004	0·0002	0·00081	0·0022
CuO . . .	0·0200	0·0160	0·0043	0·01167	0·0130
ZnO . . .	0·0052	0·0070	0·0010	0·00638	0·0049

Some zinciferous clays, called *tallow clays*, containing the eq. of 4 up to 56 per cent. of zinc oxide, occur in Missouri, Kansas, and Virginia.[4] Zinc has been reported by E. Manasse,[5] and H. Ungemach in *tetrahedrite*; by F. Mattonet and J. H. L. Vogt in *fahlerz*; by V. M. Goldschmidt, and C. Frenzel, in *argyrodite* of Bolivia; by A. de Gramont in *silver-glance*; and E. Manasse in *chrysocolla* of Campiglia. Zinc has also been reported in slags from lead and iron works by A. Stelzner, J. J. Porter, and H. Fettweis; and in blast furnace gases by E. Jensch, and A. Vita. O. Grass found cadmium in the flue-dust of a roasting furnace using Zwickau coal; and also in a lead furnace of Corphalie. P. Soltsien, and W. D. Harkins and R. E. Swain found zinc in the atm. about zinc smelters. A. Jorissen and E. Prost found zinc in the soils of Lüttich, and A. Jorissen, and P. Soltsien noted the transport of zinc from the soil to buried corpses in the cemeteries. L. Dieulafait also found zinc in the drainage from many soils. Zinc was found in the volcanic products at Soma (Vesuvius) by A. Scacchi; and by E. Casoria in the sublimation products of Vesuvius. Spectroscopic observations led J. N. Lockyer,[6] and M. N. Saha, C. A. Young, C. C. Hutchins and E. S. Holden, A. C. Jones, and H. Kayser and C. Runge to infer that zinc and cadmium are present in the sun.

The ores of zinc are widely distributed, and they are common in mines furnishing various base metals, and more particularly they are found associated with the ores of lead, silver, and copper.[7] Most of the old calamine (zinc carbonate) mines are exhausted, and more complex ores have now to be treated for zinc. The more important deposits of zinc—illustrated by the chart, Fig. 2—contain ores so complex that they present rather difficult problems to the metallurgist.

Zinc ores occur and have been mined in many parts of **Europe**—for instance, in the United Kingdom in Cumberland, Isle of Man, Flintshire, Cardiganshire, Dumfriesshire, Lanarkshire, Shropshire, and elsewhere. Germany ranks as a second largest producer, after the United States. The most important deposits are in Upper Silesia, while smaller deposits occur in Rhineland, Westphalia, Nassau, Harz, etc. In Greece, the Laurium mines are of great antiquity; in Italy, the Sardinian mines are unusually rich, and there are also deposits in Lombardy, Piedmont, and Tuscany. Most of the zinc ore mined in Spain comes from Murcia and Santander, while smaller amounts come from Teruel. The Ammeberg mines in Nerike, Sweden, are important, and deposits also occur in Orebro and Kopparberg districts. In Norway, deposits occur at Haderland, Sadon, and Primorsk. The more important deposits in France are at Malines (Gard), Pierreflitte (Hautes Pyrenées), Bulard de Santein, St. Lary (Ariége), Planisles (Lot), Bleymard (Lozière) and Bormettes (Var). The chief deposits in Belgium are at Bleyberg, Vieille Montagne, and Moresnet; those at Welkenrodt, Nouvelle, Montagne, Corphalie, and Philippeville are the most important. The more important deposits in the old Austria-Hungary, in South Carinthia, Styria, and Tyrol. In

Asia, deposits occur in India at Bawdwin, Mohocheng, Udepur, and Sirmur; in the Hunau province in China; at Kamioka (Hida), Uzen, Tsuchima, Etchu, Echizen, and Bizen in Japan; Ridder Mine (Altai Mountain) in Siberia; at Trang, Tonkin, Than Mai, Yen Liuh, Brizard in Indo-China. In **Africa**, there are deposits at Hammam N'Bails, Aïn Arko, Sakamody, Guerraouma, and R'Arbu in Algeria; Sidi-Ahmet, Fedj-el-Adoum, Zaghouan, and El-Akhouat in Tunis; at Gebel Rosâs in Egypt; and in Nigeria, Rhodesia, and the Transvaal. The United States of **America** is the largest producer of

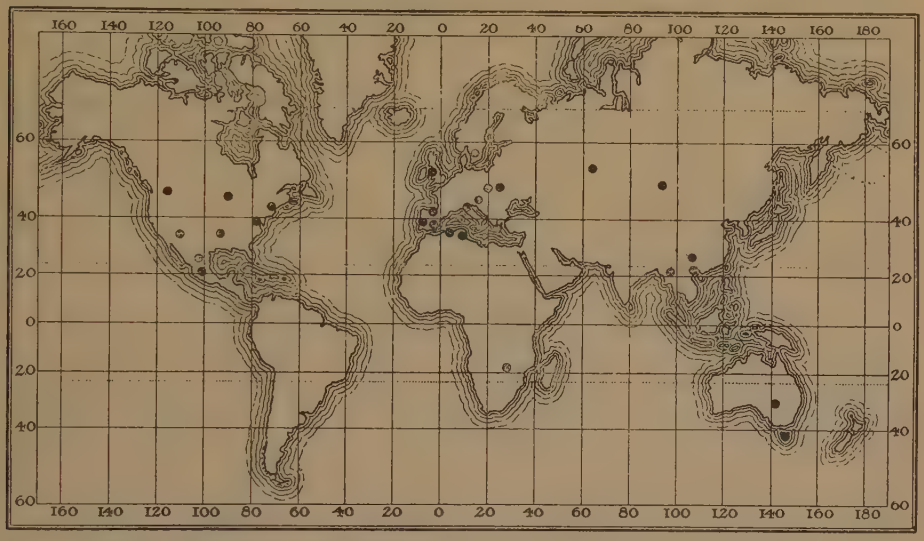

FIG. 2.—Geographical Distribution of the Chief Deposits of Zinc Ores.

zinc and spelter, and important deposits occur in Missouri, Colorado, Montana, Wisconsin, New Jersey, Idaho, Kansas, Utah, Oklahoma, Nevada, Arizona, New Mexico, Tennessee. In Canada there are deposits in British Columbia, Ontario, Nova Scotia, and Newfoundland; at Huanchaca in Bolivia; and at Chahuila, Chihauhau, San Luis Potosi, Tamaulipas, and Nuevo Leon in Mexico. There is a most important deposit of zinc and lead ores in the Broken Hill district of New South Wales, and at Mount Black and Mount Read in Tasmania, **Australasia**; Burketown in Queensland; and at Collingwood, Thames district, in New Zealand.

The World's production of zinc (spelter) is estimated in English tons (2240 lbs.) as:

1845	1855	1865	1875	1885	1895	1905	1913	1919
29,000	70,000	98,000	166,000	294,000	406,000	643,906	985,142	602,581

The output of spelter in metric tons (1000 kgrms.=2204·6 lbs.) for 1913 was:

U.S. America.	Germany.	Belgium.	France and Spain.	Great Britain.	Holland.	Austria and Italy.
320,283	283,113	197,703	71,023	59,146	24,323	21,707

with Norway, 9287; Russia, 7610; and Australia, 3724 metric tons. This distribution of the World's production [8] is almost certain to be considerably altered when the markets are in a state of equilibrium after the disturbances due to the Great War. The highest and lowest prices of commercial zinc per ton were:

	1900	1905	1910	1912	1914	1915	1920
Lowest .	£18 10*s.*	£23 5*s.* 0*d.*	£21 12*s.* 6*d.*	£25 0*s.* 0*d.*	£21 6*s.* 3*d.*	£28	£22½
Highest .	£22 15*s.*	£29 2*s.* 6*d.*	£24 5*s.* 0*d.*	£27 12*s.* 6*d.*	£34 0*s.* 0*d.*	£120	£62½

The principal ores of zinc treated commercially are: zinc sulphide, **zinc blende**, or, as it is called in the United States, **sphalerite**. This ore is fairly widely distributed, and is associated with more or less galena, iron pyrites, cadmium and manganese sulphides, as well as magnetite, hæmatite, silver, etc., and occasionally small traces of indium, gallium, thallium, and gold. While the pure zinc sulphide, ZnS, contains 67·15 per cent. of the metal in the ideal case, the blende which is treated by the smelter has between 35 and

55 per cent. of metal. The residues, after the zinc has been separated, can often be profitably worked for lead and silver. Zinc blende is usually black or brown in colour, and the miners in some districts then call the mineral *black jack*; if the blende is yellow, it is sometimes called *resin blende*; white, red, or green blende is not common. A curvilaminar variety is called *Schalenblende*; a reniform variety, *Leberblende*, and there are also varieties *Blätterblende*, *Faserblende*, *Strahlblende*, etc. It sometimes occurs crystallized in the cubic system. A variety of zinc blende with over 10 per cent. of ferrous sulphide, and may be up to the eq. of FeS.2ZnS, is called *marmatite* from Marmato; and a fibrous form of zinc blende, called *wurtzite*, crystallizes in the hexagonal system. An oxysulphide, approximately ZnO.4ZnS, of little more than mineralogical interest, is called *voltzine* or *voltzite*.

Zinc carbonate, **zinc spar**, or **calamine**, or, as it is called in America, **smithsonite**; and in Germany, *Galmei*, was one of the earliest ores to be worked for zinc. The miners in some districts call this ore *dry bone*. In the ideal case, zinc carbonate, $ZnCO_3$, contains 52 per cent. of metal but ores with as little as 13 per cent. of zinc are said to have been worked in Silesia. The impurities are mainly silica, lime, and iron, cadmium, and manganese carbonates. The mineral is white, or grey, tinged green or brown. It generally occurs massive with an imperfectly conchoidal fracture and vitreous lustre. Rhombohedral crystals are comparatively rare. A variety with over 20 per cent. of iron carbonate is called *monheimite*. The basic carbonate—*zinconise*, **zinc bloom**, or **hydrozincite**, $ZnCO_3.2Zn(OH)_2$—contains about 57 per cent. of metal; it is white or yellow in colour, and usually occurs massive. A variety with copper carbonate is called *green calamine* or *aurichalcite*.

Thermochemistry throws some light on the occurrence of certain calcium, magnesium, and zinciferous minerals. The sum of the heats of formation of zinc sulphate and calcium carbonate is greater than of zinc carbonate and calcium sulphate; the formation of zinc carbonate and magnesium sulphate is accompanied by the evolution of more heat than zinc sulphate and magnesium carbonate. Hence, other things being equal, zinc sulphate is more likely to be found in limestone rocks and zinc carbonate in dolomitic or magnesian rocks.

Zinc silicate, Zn_2SiO_4, or $2ZnO.SiO_2$, is called **willemite**, and in the ideal case, it has the eq. of 58·1 per cent. of metal, but the presence of manganese and iron lowers the proportion considerably. A flesh-coloured variety with 5 to 12 per cent. of manganese is called *troosite*. The silicate is reduced to the metal by heating it with carbon. The mineralogist's name *calamine* [9] has been applied to both the carbonate and silicate, and some confusion has in consequence resulted. It has been argued that the term *calamine* is derived from the Hindu *calaëm*, which is related to the Arabic word *climia* or *calimia* used for what is called calamine.[10] Willemite is yellow or brown in colour. The hexagonal crystals have a sp. gr. 3·9 to 4·2; hardness, 5 to 5·5. The hydrated silicate, **hemimorphite, electric calamine**, or, in the States, simply calamine, $Zn_2SiO_4.H_2O$, contains in the ideal case 53·7 per cent. of metal. This ore is not nearly so widely distributed as the sulphide or carbonate. The deposits in Aix-la-Chapelle and Moresnet (Belgium) are virtually exhausted, but there are extensive deposits in Virginia and Missouri. The Virginian deposits furnish a high-grade metal when treated by the distillation process of extraction. This mineral occurs massive with a subconchoidal fracture, or in rhombohedral crystals. The colour is white or yellowish-brown, and it sometimes has a green or blue tinge.

Native zinc oxide, *red zinc ore*, or **zincite**, ZnO, contains in the ideal case 80·2 per cent. of metal. It usually occurs massive; hexagonal crystals are rare. The colour is deep red, but if the ore occurs in thin scales, it is yellow by transmitted light. **Franklinite** is a kind of mangano-zinc ferrite, $R''O.R_2'''O_3$, or $R_2''(R'''O_2)_2$, where R'' represents Zn, Fe″, or Mn″, and R''' represents Fe‴ or Mn‴. Franklinite contains from 12 to 18 per cent. of zinc. It occurs in greyish-black octahedral (cubic) crystals. Workable deposits of franklinite and zincite are almost exclusively confined to the New Jersey district (U.S.A.). Franklinite is usually treated for zinc oxide, not for the metal.

In addition to these ores, there are other minerals of less importance—for instance, the anhydrous sulphate, **zincosite**, $ZnSO_4$; the hydrated sulphate **goslarite**, $ZnSO_4.7H_2O$, occurs in rhombohedral crystals; the aluminate, or **gahnite**, or **zinc spinel**, $ZnO.Al_2O_3$, in cubic crystals; the arsenate, $Zn_3(AsO_4)_2.Zn(OH)_2$, or **adamite** in rhombic crystals; **hopeite** is a hydrated zinc phosphate; etc.

Most zinc ores contain some cadmium, and in the extraction of zinc the cadmium accumulates in the flue-dust of the zinc furnaces. Small quantities of cadmium almost invariably accompany calamine and zinc blende. The highest value 3·4 per cent. was reported by R. Biewend [11] in the zinc blende of Eaton (U.S.A.); F. L. Bartlett found cadmium in the zinc blende from Leadville. F. Stromeyer found 2 to 3 per cent. in the blende of Przibram. C. Frenzel reported 1·136 per cent. in the blende of Nuissière; A. Damour, 0·13 to 0·21 per cent. in the zinc blende of Belgium; and E. Jensch, between 0·04 and 0·30 per cent., or on the average 0·102 per cent. of cadmium in the blende of Upper Silesia. According to E. Jensch, the

highest quantity observed in the zinc blendes of Härz, Saxony, Bohemia, Hungary, Sweden, and Norway is 0·4 per cent. Cd. C. Rimatori found up to 1·66 per cent. of cadmium in 15 samples of zinc blende from Sardinia ; E. D. Clarke found cadmium in the zinc silicates of Freiburg and of Derbyshire ; in the zinc carbonate of Mendip, Derbyshire, and Cumberland, but not in specimens from Holywell, or from Hungary. A. Schmidt, and J. R. Blum found 1·58 per cent. of cadmium in calamine from Wiesloch ; R. Bunsen reported cadmium in zinc sulphate from Härz.

Cadmium occurs as **greenockite,** cadmium sulphide, CdS, usually as a bright yellow powder on zinc blende ; hexagonal crystals are rare. The Arkansas and Missouri smithsonites are sometimes coloured with greenockite ; a cadmiferous zinc blende with up to 5 per cent. of cadmium and with a reddish colour is called **przibramite.** The basic carbonate **otavite** has 61·5 per cent. Cd, according to O. Schneider ; and the crystallized oxides are rare minerals.

W. F. Hillebrand [12] reported 0·10 per cent. of cadmium and 22·31 per cent. of zinc in the water of a spring on Shoal Creek (Missouri) and 0·37 per cent. of zinc in the water from Mountain view mine, Butte (Montana) ; C. P. Williams reported 0·02 and 0·09 per cent. of cadmium and 10·74 and 24·80 per cent. of zinc in two mine waters from the Missouri zinc region ; M. Gläser and W. Kalmann, 0·06 per cent. of zinc in the water from Roncegno (Tyrol) ; and E. Ludwig, 0·30 per cent. of zinc in a spring water at Srebrenica (Bosnia). Several analyses of mine waters have been compiled by F. W. Clarke. G. Massol reported the presence of zinc in separations from the thermal waters at Uriage (Isère) ; and F. Henrich in the sinter from the Alder spring at Wiesbaden. The presence of zinc in sea-water was reported by L. Dieulafait—0·0016–0·0020 grm. per cubic metre in the waters of the Mediterranean. A. Goldberg found zinc oxide in a boiler deposit.

The ashes of plants [13] grown on zinciferous soils have been reported as containing up to 30 per cent. of zinc oxide. M. Javillier, and T. Richardson reported the presence of zinc and cadmium oxides in coal ash—*e.g.* the ash of coal from Berwick (Scotland) contained 2·03 per cent. ZnO, and 1·42 per cent. CdO. E. Jensch found 0·0033 per cent. of cadmium in the ash of a coal from Upper Silesia ; G. Benz found zinc in fruit juices, and R. Bodmer, in wine ; P. Soltsien found 0·0067 per cent. in apple syrup. D. Spence found zinc in indiarubber. H. Claassen found zinc in the boiler deposit of a sugar works ; and G. Lechartier and F. Bellamy,[14] in several plants, *e.g.* in barley, maize, wheat, beans, vetches, clover, beet-root, etc. According to G. Lechartier and F. Bellamy, and F. Raoult and H. Breton, the human liver may contain normally 10–76 mgrms. of zinc per kgrm., and L. van Itallie and J. J. van Eck found 17 to 79·6 mgrms. per kgrm. H. Matzkewitsch said that normally zinc is not present in the healthy organism. G. Lechartier and F. Bellamy also reported zinc in calves' liver, ox flesh, hens' eggs, etc. C. B. Mendel and H. C. Bradley also reported zinc to be a normal constituent of the liver of the sycotypus (mollusc) and found 15 per cent. in the total ash, and 1·2 per cent. in the dry tissue. V. Birckner found that baker's yeast, wheat, oats, corn, barley, rye, and rice contained 15 to 415 mgrms. Zn per 1000 grms. of fresh substance ; ordinary market milk, 4·2 mgrms. per 1000 grms. ; and human milk, 6 to 14 mgrms. About 0·005 per cent. of zinc occurred in the yolk of hens' eggs, and virtually none in the white part. From its constant occurrence in cows' and human milk it is inferred that this element exerts an important nutritive function which has not been yet discovered. R. S. Hiltner and H. J. Wichmann found zinc to be universally present in oysters of the Atlantic waters to the extent of 0·0260 to 1·300 grms. of zinc per kgrm.—average 0·457 grm.

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§ 3. The Extraction of Zinc

The peculiar physical and chemical properties of zinc render the extraction of the metal from its ores somewhat costly, but the process is satisfactorily remunerative with high-grade ores containing a relatively large proportion of the metal.[1] Hence, low-grade ores are enriched by a preliminary process of conc. to remove gangue or worthless material, leaving about 50 per cent. zinc, before they are smelted.

Dry process of zinc extraction.—The operations involved in the dry process of extraction are, (i) the roasting or calcination of the ores ; and (ii) the reduction of the roasted ores in a distillation furnace, by carbon at a temp. above the b.p. of zinc, 940°.

1. *The roasting of zinc ores.*—Calamine is roasted so as to drive off the carbon dioxide and water, and leave behind zinc oxide ; hemimorphite may be calcined to drive off the combined water and leave zinc silicate behind ; and zinc blende may be roasted to convert it into the oxide, and at the same time drive off as much antimony and arsenic as possible : $2ZnS+3O_2=2ZnO+2SO_2$. If the roasting of the blende is conducted at a low temp., a comparatively large amount of zinc sulphate is formed : $4ZnS+7O_2=2ZnO+2ZnSO_4+2SO_2$; at a higher temp. most of the sulphate is decomposed, forming the oxide : $2ZnSO_4=2ZnO+2SO_2+O_2$. It is necessary to convert the sulphide to the oxide because if converted to the sulphate, the latter would be reduced to the sulphide by the carbon in the distillation retort, and the sulphide is not reduced to the metal to any appreciable extent. The roasted ore contains about one per cent. of sulphur. The relative proportions of sulphide, sulphate, and oxide in a sample of roasting blende removed from the calcination furnace at four different stages in the operation, are, according to C. Schnabel :

	Beginning.	I.	II.	III.	IV.	End.
Zinc sulphide .	83	70·5	51·5	23·2	8·6	1·9
Zinc sulphate .	0	3·7	4·2	12·3	6·2	5·9
Zinc oxide .	0	15·2	38·0	57·8	75·5	81·0

A large variety of roasting furnaces of the reverberatory type are employed in which the charge is agitated mechanically or by hand. In the better class of installation, the sulphurous gases from the roasting blende are used for the manufacture of sulphuric acid.[2]

2. *The reduction and distillation of the metal.*—The volatility of zinc at bright red heat, enables the metal to be extracted from the ore by distillation processes. The powdered oxide is mixed with about half its weight of anthracite coal, *i.e.* a quantity four or five times in excess of theoretical requirements : $ZnO+C\rightarrow Zn+CO$, and heated in closed fireclay retorts to which condensers are attached. The retort is heated to 1200°–1300°. The heat has to pass through the walls of the retort, which are poor heat conductors. The retorts are accordingly made comparatively small. The zinc oxide is reduced by the carbon or carbon monoxide at a temp. higher than the b.p. of the metal. In consequence, as soon as the metallic zinc is reduced, it is vaporized and the vapour is condensed to a liquid in fireclay, or iron receivers or condensers adapted to the retorts Carbon monoxide escapes. Zinc silicate ores—willemite and hemimorphite—are also reduced by carbon, but at a higher temp. than is required for the oxide. There are some interesting phenomena associated with the process.

The vapour of zinc must be condensed at a temp. well under the b.p. and over the m.p. of the metal. When the zinc vapour is condensed below about 415°, it forms a powder—called *zinc dust*, *blue powder*, *zinc fume*, or *poussière*[3] which is usually a mixture of 8 to 10 per cent. of zinc oxide with metallic zinc ; if the temp. of the receiver exceeds 550° the vapour does not condense at all. Consequently, the permitted range for the temp. of the condenser is comparatively narrow—according to L. V. T. Lynen, 415° to 550°.

The reduction of the oxide to the metal is difficult. Assuming that the heat of formation of zinc oxide is 86 Cals.; of carbon monoxide, 29 Cals.; and of carbon dioxide, 97 Cals.; it follows by Hess' law that $ZnO+C=CO+Zn$—57 Cals. M. Bodenstein and F. Schubart[4] gave 89·6 Cals.; $2ZnO+C=2Zn+CO_2$—75 Cals.; M. Bodenstein and F. Schubart gave $2ZnO+C=2Zn_{vapour}+CO_2$—141·9 Cals. at 1000°; and $CO_2+C=2CO$—39 Cals.; and $ZnO+CO=Zn+CO_2$—19 Cals. This means that in the reduction of zinc oxide by carbon, the heat absorbed is 57 Cals., when the products of the reaction are taken to be cold; otherwise, an allowance must be made for the change in the sp. ht. of the different substances concerned in the reaction.

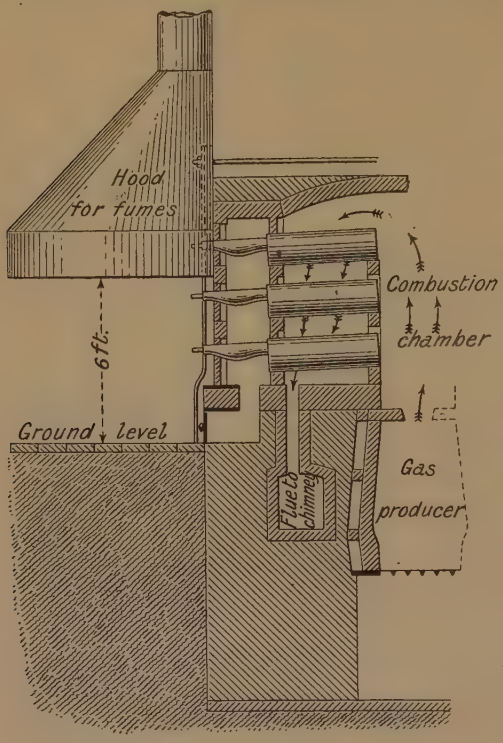

Fig. 3.—Transverse Section of half a Rhenish Zinc 3-tier Furnace.

Although the reduction of zinc oxide by carbon can be detected below 700°, the reaction is so slow that temp. in the vicinity of 1300° are actually employed. M. Bodenstein and F. Schubart measured the temp. at which a mixture of zinc oxide and carbon is converted into zinc vapour and carbon monoxide at 28 mm., 87 mm., 266 mm., and 760 mm. press. The approximate temp. is 1030° in agreement with 1022°, by W. McA. Johnson. The latter also found the temp. of calcination of the zinc oxide affects the temp. of reduction. Thus, zinc oxide calcined at 1100° and at 1300° is reduced by soft coke at 1048° and 1061° respectively. M. Bodenstein and F. Schubart found for the equilibrium constant, K, in the reaction: $ZnO+C=Zn_{vapour}+CO$, when p_1

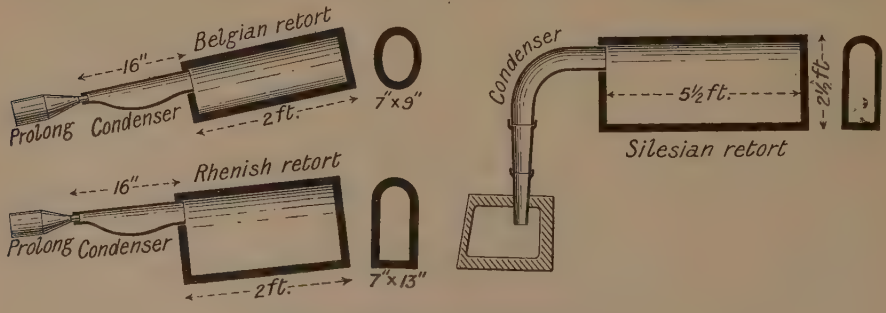

Fig. 4.—Three Types of Zinc Retort.

and p_2 respectively denote the partial press. of zinc vapour and carbon monoxide, $K=p_1p_2$, F. Schubart found

	596°	627°	665°	695°	729°	756°	795° C.
p_1	2·3	5·15	12·45	27·7	60	92	156
p_2	2·3	5·15	12·45	27·7	100	295	1097
K	$1·8\times10^{-9}$	$8·4\times10^{-9}$	$4·5\times10^{-8}$	$2·5\times10^{-7}$	$1·5\times10^{-6}$	$6·6\times10^{-6}$	$3·9\times10^{-5}$
Q Cals.	—	—77	—74	—92	—112	—110	—98

where Q denotes the heat of the reaction. The temp. of the reaction is 921° when the press. is 28 mm.; 945° when 86 mm.; 982° when 266 mm.; and 1010° when 760 mm. The thermal value Q of the reduction of zinc oxide by carbon, calculated from the equation $\log K_2 - \log K_1 = -4{\cdot}571Q(T_1^{-1} - T_2^{-1})$, between 1012° and 982° is −219·3 Cals.; between 982° and 946°, −185·6 Cals.; between 946° and 908°, −151·3 Cals.; and at ordinary temp., −89·6 Cals. At 1000°, $K=63$. It is also estimated that $\log_{10} Kp = -0{\cdot}2188 \times 89600T^{-1} + 1{\cdot}75 \times 2 \log_{10} T + 6$, approximately. An exact calculation was not made because of the want of knowledge of the equilibrium between carbon, carbon monoxide, and carbon dioxide with sufficient accuracy. M. Lemarchands showed that in an atm. of nitrogen, zinc oxide is readily reduced directly by carbon without the necessary intermediate formation of carbon monoxide. The amount of carbon entering into the reaction is intermediate between the amounts necessary for the two possible actions. $ZnO+C=Zn+CO$, $2ZnO+C=2Zn+CO_2$. This is explained on the grounds that the reduction of zinc oxide by carbon monoxide, $ZnO+CO=Zn+CO_2$, takes place with a velocity superior to that of the reduction of carbon dioxide by carbon. This is possible, since the first action commences at 350°, and the second only at 400°. According to E. Jänecke, if solid zinc oxide and carbon be added to molten zinc in a space from which the air has been exhausted, then, at temp. above the m.p. of zinc, an equilibrium will be established between the two solid phases and one liquid phase and one gaseous phase. It is a univariant equilibrium, since the four phases may be formed from three independent components, and hence the press. and composition of the gas will be constant at a definite temp. and will vary with the temp.

In the reduction of the common metal oxides by carbon monoxide, the reaction : $MO+CO \rightleftharpoons CO_2+M$, is reversible, but the conc. of the carbon dioxide must be very great before the back-reaction—reduction of carbon dioxide and oxidation of the metal—sets in with an appreciable velocity; but with zinc vapour, the back-reaction with carbon dioxide : $Zn+CO_2 \rightleftharpoons CO+ZnO$, occurs with a comparatively small conc. of carbon dioxide. Zinc vapour can be oxidized by carbon dioxide so that an excess of carbon must be present in the retort to maintain an atm. of carbon monoxide and keep the conc. of carbon dioxide very small by the reaction $C+CO_2=2CO$. According to O. Boudouard, carbon monoxide at 1000° acts as a reducing agent until about 0·1 per cent. of carbon dioxide is present and the system $ZnO+CO \rightleftharpoons Zn+CO_2$ is in equilibrium; any further proportion of carbon dioxide means that the back-reaction—oxidation of zinc—will occur. At 1125°, the equilibrium proportion of carbon dioxide is 0·2 per cent., and at 1500°, 0·76 per cent. The mean of seven analyses of the gases issuing from zinc retorts during distillation is : Carbon dioxide, 0·54 per cent.; carbon monoxide, 96·02; hydrogen, 2·56; and nitrogen, 0·74 per cent.

If the vapour of zinc be too much diluted with other gases, it can condense only to zinc fume, and not into fluid metal. The greater the proportion of these gases the greater the proportion of zinc fume. This fact, and the back reaction, indicated above, explains why all attempts to reduce the oxide in reverberatory and blast furnaces have not been satisfactory. Either zinc oxide or the troublesome zinc fume is obtained.

Three types of retort-furnace are used—the Belgian, the Silesian, and the so-called Rhenish, which is really a modification of the two former, and is perhaps the favourite type. Half a transverse section of a Rhenish furnace is shown in Fig. 3. It is supposed to be fired by gas made in a central gas producer. Each retort, with all three types, has three parts : the body, the condenser, and the prolong or nozzle. The smallest retorts are used with the richest ores, and conversely. There is, however, a considerable variation in the shape and size of the retorts used by different smelters, as is also the case with the arrangement of the retorts in the furnace. In the Silesian process, the typical retorts are comparatively large, Fig. 4, and might be termed muffles rather than retorts. There was only one tier of retorts in the original Silesian furnaces, but two and even three tiers may be used in a modern bank of retorts. The Belgian retorts are usually elliptical, rarely cylindrical, Fig. 4, and they are arranged in three to five tiers each containing 6 to 8 retorts.

The mode of arrangement is illustrated in Fig. 3. The Rhenish retorts are rather larger than the Belgian, and smaller than the Silesian, Fig. 4, and they are arranged in two or three tiers in double furnaces with 60 to 100 retorts on each side, Fig. 3. Some of the larger modern furnaces have over 1000 retorts. The furnaces are usually gas fired with or without regeneration; sometimes they are coal fired.

In the typical process, the retorts are recharged every 24 hrs. The retorts are cleaned and patched, or new retorts are substituted for defective ones. In some works special machines are employed for discharging the retorts. The well-mixed charge, slightly damped, is introduced by hand scoops. The condensers are luted on, and when the flames of the carbon monoxide burning at the mouths of the condensers are tinged bluish-green by zinc, the prolongs are fitted on, and the temp. of the retorts gradually raised. Molten zinc accumulates in the condensers, and zinc fume in the prolongs. The liquid zinc in the condensers is drawn off in the hand or other ladles from time to time. The appearance of the carbon monoxide flame burning at the exit tells the operator when the distillation is finishing. When completed, the spent residues are removed, and the cycle begins anew. The progress of the distillation can be observed through the open condensers of the Belgian and Rhenish systems. The whole cycle of operations occupies about 24 hrs. of which 19 hrs. are taken up by the distillation.

As previously indicated, the term *spelter* is applied in commerce either to all ingot zinc, or to a metal containing up to about 99·8 per cent. of zinc. If the metal contains over this amount of zinc, it is called *fine zinc*. The term *zinc* is usually reserved for the rolled metal, and for use in chemical and mineralogical nomenclature. Commercial spelter contains from 0·06 to 2·55 per cent. of lead; 0·01 to 0·26 per cent. of iron; 0·005 to 0·09 per cent. of cadmium; and up to 0·07 per cent. of tin.[5] The lead is derived from the ores, and it distils over with zinc. The amount of lead in zinc cannot be reduced much below 0·2 per cent. by distillation; there appears to be a constant boiling mixture formed as in the case of aq. soln. of hydrochloric acid, etc. Good spelter should not contain over 1·5 per cent. of lead. The iron in spelter does not come from the ores, but is taken up when zinc is remelted in iron vessels, or stirred with iron rods. The presence of iron reduces the malleability of the metal. Good spelter does not contain more than 0·05 per cent. of iron. Probably all zinc contains some cadmium, and this element is not considered particularly deleterious, but it makes the metal more brittle, and when used for galvanizing, the presence of cadmium makes the coating more liable to peel off—this is serious on telephone and telegraph wires when the sharp bends make the coating crack or peel, exposing the underlying metal. It is derived from the ores, and distils over with the zinc. Traces of arsenic are usually present. Eight samples of Belgian, Silesian, Rhenish, and American spelters contained from 0·002 to 0·060 per cent. of arsenic; up to 0·02 per cent. of antimony; from 0·001 to 0·070 per cent. of sulphur; from 0·001 to 0·178 per cent. of carbon;[6] from 0·002 to 0·137 per cent. of silica; from 0·0002 to 0·112 per cent. of copper; and in some cases slight traces of bismuth.

Many studies and modifications of the carbon reduction and distillation processes have been made.[7] Other reducing agents have been suggested—W. E. Blass[8] used carbon monoxide; H. Goldschmidt, aluminium; A. G. Betts, silicon or a silicide, alloys of aluminium, calcium, or magnesium, or a carbide; L. M. Bullier, E. W. von Siemens and J. G. Halske, and O. Frölich, calcium carbide. Instead of producing zinc directly, processes have also been devised for recovering zinc from alloys with other metals—lead, nickel, etc.—and also from slags.[9]

The blast furnace treatment of zinc ores.—Many attempts have been made to dispense with the large number of retorts employed in the ordinary distillation process, and to make the smelting a continuous process. E. F. J. Duclos[10] and F. L. Clerc proposed the use of a closed blast furnace with a hot blast, and a condensing apparatus. The latter emphasized the importance of keeping the zinc vapours diluted as little as possible with carbon dioxide, and of not cooling the

vapour below the m.p. of the metal so as to avoid the formation of blue powder. E. E. Lungwitz proposed to smelt zinc ores in a blast furnace worked under a press. of about 120 lbs. per sq. in. with the idea of raising the b.p. of the metal. O. Nagel also worked a mixture of the zinc ore with coal in a blast furnace maintained full of water gas supplied through tuyères. Spelter was successfully produced, but the losses due to the formation of too large a proportion of blue powder and zinc oxide seriously hampered the processes.

The electrical smelting of zinc ores.—C. G. P. de Laval [11] introduced the electric smelting of zinc ores in Scandinavia, about 1904. The ore of zinc may be mixed with carbon, and charged into an electric furnace in such a manner as to form on its bottom a pile or stack sloping by gravity opposite to a source of electric heat. The pile of ore is continuous into the shaft into which the ore is charged. As the ore melts on its sloping face, it flows into a depressed part of the furnace, whence the slag may be withdrawn, a fresh surface of the ore being continually exposed to the radiant heat. The volatilized zinc and the gases generated have exit by a separate outlet for condensation. The process has successfully produced good spelter at Trollhattan (Sweden), Sparsborg (Norway), Hartford (Connecticut), Nelson (British Columbia), and Hamborn (Westphalia). Many other types of electrical smelting have been proposed. Where cheap electrical energy is available, electrical smelting holds alluring promises of commercial success, but where cheap electrical power is not available the consumption of 12,000 kilowatt-hours per ton of metal is not a commercial proposition.

The extraction of zinc by wet processes.—Zinc cannot be precipitated from soln. of its salts by metals which do not oxidize at ordinary temp.; if other precipitants are used, the zinc is obtained as oxide; this must be mixed with carbon, and treated for zinc by the distillation process. The high cost of the wet processes of extraction involving the leaching of the ore for zinc salt, say sulphate, and its subsequent conversion of the sulphate to oxide, etc., was formerly prohibitive; but the growing demand for white pigments free from lead—*e.g.* lithophone, etc.—has rendered it possible to extract economically the zinc in the form of sulphate instead of as metal. The subject has been investigated by O. C. Ralston.[12] In 1851 J. Swindells proposed to roast zinc blende with sodium chloride in an oxidizing fire—*chloridizing roast*—extract the sodium sulphate, ferric chloride, and zinc chloride with water, precipitate the zinc hydroxide with lime; and then treat the hydroxide for zinc by the distillation process. A. C. Becquerel, W. Stahl, A. Gurlt, C. Höpfner, W. J. Huddle, and others have suggested modifications of the process. E. A. Parnell, and H. Pape roasted the sulphide ore to sulphate, leached with water, evaporated the pure zinc sulphate soln. to a paste, treated it with zinc sulphide, and heated the mixture to produce zinc oxide: $3ZnSO_4+ZnS=4ZnO+4SO_2$. Soln. of sodium or ammonium chloride, or a suitable halogen salt, are available for dissolving out the lead sulphate or chloride.

J. Swinburne and E. A. Ashcroft chlorinated the sulphide with gaseous chlorine at a dull red heat, and modifications have been suggested by F. W. Traphagen, F. Rickard, A. Tixier, G. Carrara, and G. Mojana. Several processes have been devised in which the oxidized or roasted ore is treated with an acid. For example, F. M. Lyte, J. W. Worsey, J. Asbeck, E. Ferraris, P. Hart, etc., extracted the roasted ore with sulphuric acid; F. M. Lyte, etc., with hydrochloric acid; and E. A. Ashcroft, with a soln. of ferric chloride. C. Kellner, G. Dautin, C. Höpfner, V. Lindt, and H. Brandhorst, H. L. Sulman, used sulphurous acid. Soluble zinc hydrosulphite, $Zn(HSO_3)_2$, is formed, and the soln. is pumped into a tank where zinc sulphite, $ZnSO_3$, is precipitated. This is roasted to oxide, and the sulphur dioxide used for the treatment of more ground ore. C. Schnabel, F. Ellershausen and R. W. Western, J. Wojtasiewitsch, etc. extracted the zinc oxide from the roasted ore by an ammoniacal soln. of ammonium carbonate. F. E. Elmore extracted lead and zinc from ores, etc., in which these metals occur as sulphides, by heating with an acid agent—sulphuric acid, or a soln. containing sulphuric acid or an alkali hydrosulphate, hydrochloric acid, etc.—which converts the lead into a soluble compound while the zinc sulphide remains unattacked.

Electrolytic processes for the extraction of zinc.—Many processes [13] have

been devised in which the roasted zinc ore is treated with a solvent, and the zinc precipitated electrolytically from the soln., but (i) the high consumption of electrical energy necessary to deposit a strongly electropositive metal like zinc from its aq. soln. using an insoluble anode; (ii) the difficulties which are encountered at the cathode in preventing the formation of spongy zinc; and (iii) the difficulties in roasting, lixiviating, and purifying the liquors so as to produce an electrolyte of constant and definite composition, have all militated against the electrolytic zinc industry. In 1862, J. Dickson described a process for obtaining zinc from its ores by electrolysis; he proposed to deposit this metal from acid, aq., or alkaline soln. obtained by leaching roasted zinc ores, or by acting on the raw ores with acids. The suggested process attained no commercial success. In 1881, C. Luckow, and shortly afterwards C. Blas and E. Miest, devised processes for the direct extraction of zinc by utilizing zinc ore as the anode of an electrolytic bath—C. Luckow used a soln. of zinc and sodium chlorides as electrolyte, C. Blas and E. Miest used zinc nitrate. L. Létrange proposed to roast zinc blende at a low temp. to convert the sulphide to sulphate. The zinc was leached out with dil. sulphuric acid, and the soln. on electrolysis furnished zinc and sulphuric acid. The latter was to be used again in the process. E. W. von Siemens and J. G. Halske tried (i) leaching the calcined ore with acid ferric sulphate liquor, when zinc sulphide and oxide were dissolved—on electrolysis, the lixiviating liquor was regenerated; the zinc was spongy, and contaminated with much iron; and (ii) leaching with alum soln. when soluble basic aluminium salts were produced—on electrolysis, no acid was set free, but the lixiviating liquor was regenerated; the zinc deposit was not satisfactory. The best results were obtained by (iii) leaching with dil. sulphuric acid. Platinum electrodes, apart from their first cost, slowly dissolved in the technical liquor; and fouled the electrolyte; ferric oxide proved useless; but electrolytically deposited lead dixoide proved very stable chemically. V. Laszscynsky extracted roasted blende with the spent acid liquor from the electrolysis vat; dissolved ferrous iron was oxidized by air or potassium permanganate and precipitated by zinc oxide. Copper, arsenic, and cadmium were removed by hydrogen sulphide. The electrolysis current was 1500 amps. and 4 volts. In C. Höpfner's process, modified by Brunner-Mond Co. at Winnington, it is said that the roasted ore is mixed with water and ground to a pulp, which is treated, in the presence of carbon dioxide, with the calcium chloride waste-liquor from the ammonia-soda process: $ZnO+CaCl_2+CO_2 \rightarrow CaCO_3+ZnCl_2$. The iron, manganese, and electronegative metals are electrolyzed between graphite anodes, and rotating iron cathodes. The chlorine evolved at the anode is used in making bleaching powder; the zinc is said to be of 99·95 to 99·98 per cent. purity.

Zinc is far more electropositive than hydrogen, and it might be anticipated that cathodic deposition would not be possible in the presence of an appreciable amount of free acid; but highly purified zinc is but little affected by acids—even 10 per cent. sulphuric acid. Zinc can be successfully deposited from acid soln. when a high current density is used because of the high over-voltage necessary for the discharge of hydrogen from a zinc surface; and from an electrolyte containing zinc and hydrogen ions, the former is preferentially deposited. If the zinc be of a low degree of purity, the hydrogen over-voltage is low, and the zinc dissolves—iron, silver, nickel, copper, or arsenic act in this way and favour the dissolution of the zinc; while tin, cadmium, and lead are less active. Similarly if the electrolyte contains one of these metals, the discharge of hydrogen is favoured and the deposition of zinc hindered. A high current density raises the over-voltage, likewise also a low temp. Hence, these two conditions, coupled with a high zinc conc. and low acid conc. in the electrolyte, favour the deposition of zinc.

The zinc should deposit as a compact, coherent, greyish-white, finely crystalline mass with a slight tendency to give irregular growths at the edges; but it is very prone to form a spongy dark-coloured voluminous mass which is liable to cause short-circuiting, and introduce difficulties in melting owing to its enclosing some

electrolyte, and to its liability to oxidation. The conditions necessary for the production of a satisfactory deposit of zinc have been made clear by the work of M. Kiliani, F. Mylius and O. Fromm, and F. Förster and O. Günther. It is generally assumed that the formation of *spongy zinc* is favoured by the presence of zinc oxide, or basic zinc salts in the electrolyte, which disturbs the crystallization of the metallic zinc. A low acid conc. therefore favours the formation of spongy zinc. Depolarizers which form acids on reduction usually hinder sponge formation—*e.g.* hypochlorous or persulphuric acids ; on the contrary, oxidizing agents which give neutral or basic substances on reduction favour sponge formation—*e.g.* hydrogen peroxide or nitrates. Sponge formation rapidly sets in when zinc is deposited from alkaline soln., although the excess of alkali prevents the precipitation of oxide or basic salt. A. Hantzsch, however, found that alkali zincate soln. are strongly hydrolyzed, and contain colloidal zinc hydroxide.

Whatever favours the discharge of hydrogen ions tends to produce spongy zinc, and once the sponge is deposited, the discharge of the $H^{\cdot}$-ions will increase since the over-voltage of hydrogen with zinc sponge is less than with the massive metal. A high current density and a low temp. favour the formation of a coherent deposit. The relation between the temp. and the current density—amps. per sq. dm.—required for the production of a coherent deposit of zinc, is illustrated diagrammatically in Fig. 5. Irregularities on the surface of the cathode cause the current density to fall locally. If the electrolyte be not renewed owing to poor circulation the soln. in the vicinity of the cathode is depleted of zinc ions, and there is a further fall in current density. Hence, a good circulation of the electrolyte, and the use of a moderately conc. soln. of the zinc salt—say 40–60 grms. per litre—favours the deposition of coherent zinc. The presence of an electro-negative metal in the electrolyte favours the formation of spongy zinc.

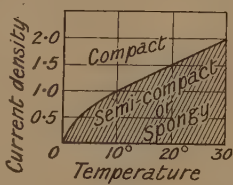

FIG. 5.—Relation between Current Density and Temperature for the Deposition of Compact Zinc.

Several works have produced zinc by an electrolytic process—*e.g.* the Anaconda Co. has an electrolytic plant producing up to 100 tons per diem ; another plant at Trail, British Columbia, can produce 40 tons per diem ; another plant is working at Risdon, Tasmania ; etc. According to F. Laist, F. F. Frick, J. O. Elton, and R. B. Caples, and S. Field, the process, in general outline, involves : (1) The *calcination* of the ores under special conditions to render the zinc soluble in sulphuric acid. (2) The *extraction* of the zinc from the calcined ore by the acid-liquor from the electrolytic cells. The crude zinc-sulphate soln. so produced contains about 10 per cent. of zinc sulphate ; 0·05 per cent. of copper ; 0·03, cadmium ; 0·10, manganese ; 0·05, iron ; 0·01–0·001, cobalt ; 0·01–0·001, nickel ; as well as a little arsenic and antimony. Most of these impurities are highly detrimental to the successful electro-deposition of zinc. (3) The *purification* of the crude liquor is therefore of vital importance. Many patented methods have been devised. (4) The *acidification* of the purified liquor is necessary for economical electrolysis. This is effected by regenerated acid, and the acid liquor from the electrolysis cells. (5) The *electrolysis* is effected with lead anodes, and aluminium cathodes. (6) The deposited zinc is easily detached from the cathodes, and melted into ingots. The silver and lead in the residues remaining after the extraction of zinc from the calcined ore may be recovered as argentiferous lead. The electrodeposition of zinc has also been discussed by J. T. Ellsworth, and W. G. Traub.

The extraction of zinc by the electrolysis of fused salts.—The production of zinc by the electrolysis of the fused chloride has been investigated on a small and on a large scale. Fused zinc chloride is the principal product of J. Swinburne and E. A. Ashcroft's [14] and C. E. Baker and A. W. Burwell's processes for the chlorine smelting of complex ores. It has also been proposed to prepare zinc chloride by the action of hydrochloric acid on the roasted ore, and to evaporate, fuse, and

electrolyze the product. The difficulties connected with the electrolysis of fused zinc chloride have been investigated by R. Lorenz and co-workers. One of the chief difficulties is the preparation of anhydrous zinc chloride in vacuo. If zinc chloride be melted in an open crucible in air, and electrolyzed between carbon electrodes, much gas is evolved at both electrodes, zinc chloride vapours are evolved, the fused mass becomes turbid and a bad conductor, and no zinc is produced. If the zinc chloride be first mixed with sodium chloride the results are better, but still very bad. The trouble is due to the presence of moisture, derived largely from the flame gases. If the flame gases have no access to the melted mass which has been heated until fuming has ceased, hydrogen and oxygen are given off when the current is first passed; gradually, however, the evolution of hydrogen slackens off, and chlorine takes the place of the oxygen. Zinc is then produced, and the liquid remains clear. Hence, the water can be removed from zinc chloride by heat and electrolysis. The zinc chloride for this purpose was prepared by R. Lorenz by conducting the last stages of the evaporation in an atm. of hydrogen chloride. J. F. L. Vogel prepared this salt by evaporation. Another difficulty is the wear and tear on the electrolytic cell when heated externally. There is also a loss due to vaporization and the formation of a metal fog studied by S. Grünauer. The formation of fog is much reduced if a mixture of zinc and alkali chlorides be used; thus, at 600°, the percentage current efficiency was:

Electrolyte	$ZnCl_2$	$ZnCl_2+KCl$	$ZnCl_2+NaCl$	$ZnCl_2+1{\cdot}2NaCl$
Current of efficiency	73·9—75·9	92·1—94·7	83·9—89·9	89·6—91·2

R. Suchy found the e.m.f. of the cell Zn | fused $ZnCl_2$ | Cl_2 to be:

	450°	500°	550°	600°	650°
Volts	1·643	1·611	1·576	1·535	1·494

and R. Lorenz found the decomposition voltage between 500° and 600° to be 1·49 volts. If the zinc chloride contains iron, that metal is deposited before the zinc, the current efficiency is lowered, and the progress of the electrolysis disturbed. G. Gallo obtained much better results by the electrolysis of fused zinc fluoride, m.p. 734°, or of a mixture of zinc fluoride and sodium chloride melting at about 500°.

The purification of zinc.—When ordinary zinc is dissolved in acids, a black residue remains. This was observed by J. Hellot[15] in 1735, and by F. de Lassone in 1777. A. F. de Fourcroy stated that the black powder is iron carbide or plumbago; L. N. Vauquelin said the black powder is iron carbide, and L. J. Proust (1806) stated that "it is commonly thought that the black powder is charcoal or zinc carbide; it is nothing but arsenic mixed with a little lead and copper which the reducing power of the zinc precipitates in the metallic state." He also added that commercial zinc contains iron and manganese. It is thought that the precipitate produced by hydrogen sulphide, and called by L. J. Proust arsenic, was most probably cadmium, a metal not discovered until 1817. A. Vogel said the residue contains carbon, iron, and lead; J. J. Berzelius and P. L. Dulong said that the impurities in zinc are lead, tin, copper, iron, cadmium, and sulphur. A. A. de la Rive found traces of tin, lead, cadmium, and sometimes more than one per cent. of iron. G. F. Rodwell, R. Funk, G. C. Wittstein, G. Barruel, and O. L. Erdmann and R. F. Marchand obtained similar results. R. Schindler reported the presence of iron, lead, arsenic, copper, nickel, cobalt, manganese, carbon, and a little uranium, but later observers have not confirmed the presence of uranium. H. W. F. Wackenroder did not confirm the statement of K. S. L. Hermann that zinc contains cobalt, nickel, and manganese, but he found copper; nor did he find carbon or arsenic, but he admits that arsenic might be present in small quantities. A. Erdmann said that it is impossible to separate completely lead from zinc by distillation because of the partial volatilization of lead. Many reports of the presence of sulphide in zinc are based on the production of hydrogen sulphide when commercial zinc

is treated with acids—*e.g.* M. Blancard—but M. J. Fordos and A. Gélis said that "the formation of hydrogen sulphide can be attributed only to the partial reduction of the sulphuric acid by the nascent hydrogen," and subsequently V. A. Jacquelain attributed the hydrogen sulphide to the presence of sulphurous acid or other compounds of sulphur in the sulphuric acid, and doubted if the metal reduced the sulphuric acid. C. W. Eliot and F. H. Storer found every sample of zinc they treated gave hydrogen sulphide when dissolved in an acid free from sulphur, although C. J. B. Karsten, and F. Alger found samples free from sulphur. Many reports of arsenic in zinc are mal-observations due (1) to the confusion of the yellow sulphide of arsenic with the yellow sulphide of cadmium; (2) to the presence of arsenic in the acid employed for dissolving the zinc; and (3) to the use of tests of insufficient delicacy. C. W. Eliot and F. H. Storer found arsenic in the great majority of samples of commercial zinc, and traces of many impurities—carbon, sulphur, magnesium, manganese, aluminium, arsenic, antimony, cadmium, lead, iron, cobalt, nickel, bismuth, silver, and copper. F. Meyer, E. Jensch, F. Mylius and O. Fromm, A. Wagner, E. Reichardt, C. Stahlschmidt, F. Robineau and G. Rollin, G. Bonnet, etc., have also made observations on this subject. Commercial samples of zinc have approximately the composition:

	Zn	Pb	Fe	Cd	Sb, As, Sn
Electrolytic (English)	99·97	0·007	0·010	0·004	—
Spelter (Welsh)	97·22	1·30	1·42	0·03	0·01
Common spelter (English)	98·66	0·51	1·72	0·06	0·03
High-grade spelter (American)	99·96	0·02	0·02	—	—
Spelter (Silesian)	98·92	1·03	0·02	0·02	0·01

T. R. Rolfe found that between 1913–16, the different brands of spelter contained between 0·31 and 2·03 per cent. of lead, and up to 0·19 per cent. of iron. C. J. B. Karsten obtained similar results in 1842. Spelter usually contains less than 0·2 per cent. of cadmium, although the latter may rise up to 2·0 per cent. Arsenic, antimony, copper, sulphur, and carbon are usually present in too small a proportion to affect the properties of the metal. Tin, copper, and aluminium may be found in remelted spelter. The purest zinc was found by G. H. Williams, W. M. Burton, and E. W. Morley to contain carbon. C. Viollette and R. Funk said that the carbon is free, not combined with zinc as R. Schindler supposed. C. Künzel found zinc prepared from scrap-zinc contained 0·2 to 0·3 per cent. of chlorine. R. Funk found 0 to 2·5 parts of sulphur in 10 million parts of zinc probably suspended therein as zinc sulphide. K. Friedrich found small proportions of silver in zinc; and A. Streng found thallium in the zinc from Vieille Montagne. D. Pacini found that zinc is more readily freed than other metals from radioactive impurities. G. D. Scholl discussed the impurities in electrolytic zinc.

Lead in spelter is considered objectionable for many purposes. When the spelter contains 2 to 3 per cent. of lead, it is refined by liquation. A large bath—holding 20–30 tons—is kept molten for some days at as low a temp. as possible. The bulk of the lead accumulates by gravity at the bottom, and a better grade of zinc, with 0·8 to 1·0 per cent. of lead, accumulates at the top. This 0·8 to 1·0 per cent. represents the solubility of lead in molten zinc just above its m.p. The insoluble lead settles in minute globules. An alloy of iron and zinc also settles just above the lead, so that some iron is simultaneously removed from the spelter. Less fusible impurities float as a scum on the molten metal, and can be skimmed off. Re-distillation is sometimes used for recovering zinc from alloys rich in lead.

G. C. Stone has reported analyses of American spelters. In 1911, the American Society for Testing Materials suggested the following four grades of commercial spelter:

	Pb	Fe	Cu	Maximum total
A.—High grade	0·07	0·03	0·05	0·10
B.—Intermediate	0·20	0·03	0·05	0·50
C.—Special, brass	0·75	0·04	0·75	1·20
D.—Prime Western	1·50	0·08	—	—

G. C. Wittstein recommended purifying zinc by distilling the metal once or twice from a clay retort; V. A. Jacquelain distilled the metal in a stream of hydrogen. J. J. Berzelius and P. L. Dulong added that distillation does not remove the more volatile metals—arsenic, antimony, cadmium, and lead—and the zinc after distillation still retains these impurities. H. N. Morse and W. M. Burton distilled commercial zinc in vacuo, using a glass tube divided into three compartments. The metal was distilled from the first compartment into the second and third; when about one-fourth still remained in the first compartment, and about one-tenth had passed into the third, the operation was stopped, and repeated four times on the contents of the second compartment. The metal was spectroscopically free from lead, cadmium, tin, and indium. M. J. B. Orfila and A. Meillet fused granulated zinc with a little nitre to remove arsenic and iron. J. S. Stas removed carbon from zinc by melting it with litharge—this introduces lead into the zinc. R. Funk removed sulphur and carbon by melting the metal many times and filtering it through asbestos. R. D. Bohannon obtained iron-free zinc by reducing zinc chloride with sodium. J. W. Gunning, G. Bonnet and M. Schwake, W. Merton, and F. Stolba recommended fusing zinc with sulphur or a mixture of sulphur and sodium carbonate to remove arsenic. P. Lohmann recommended removing arsenic by fusing the metal with potassium cyanide; C. Mann, fusion with borax; F. Selmi, fusion with ammonium chloride; O. Hehner, and L. T. Thorne and E. H. Jeffers, fusion with sodium; T. l'Hôte, fusion with dried magnesium chloride; and H. Lescœur, fusion with nitre, or with zinc chloride. F. Mylius and O. Fromm said that purification by fusion with nitre or sulphur, or by distillation, is incomplete. J. Myers has claimed to have prepared zinc with but one part of impurity in 100,000 parts of metal.

Zinc of a high degree of purity can be obtained from zinc-ethyl, and when electrolyzed with platinum as anode and zinc as cathode, the electro-deposited metal contains a trace of platinum; but, by using a zinc anode, and working with a basic soln. and low current density spongy zinc is obtained, which, by many repetitions of the process, is free from foreign metals. The spongy metals should be well washed, and freed from oxide, by fusion with ammonium chloride, and finally, by sublimation in vacuo.

The electrolytic refining of zinc, using sheet zinc as cathode, and plates of the impure metal as anode, conducted as in the case of copper refining, has been only partially successful. The operation is not usually economical unless the anode slimes are rich in noble metals, as is the case with the zinc-silver alloy obtained in Parkes' process.[16] In any case, however, the economic margin is small, and the older separation by distillation has proved to be simpler and cheaper; but, for small quantities, the electrolysis of the highly purified chloride or sulphate can furnish a metal of 99·998 per cent. purity.

The extraction of cadmium.—G. Städler,[17] and F. O. Döltz and C. A. Graumann showed that when cadmiferous zinc ores are roasted, a certain amount of cadmium is lost, either by the volatilization of the oxide, or by the reduction of the oxide and volatilization of the metal. E. Jensch reports a loss of nearly 62 per cent. of the cadmium in this way. The cadmium oxide in the roasted zinc ores is reduced with the zinc in the retorts, and owing to the great volatility of the metal, the cadmium distils first, and imparts a brownish tinge to the flame of carbon monoxide burning at the mouth of the retort before the bluish-green tinge of zinc appears. Cadmium accumulates partly in the liquid zinc in the condenser, and partly in the zinc fume in the prolong. When it is desired to recover the cadmium, the fraction which collects in the condenser and prolong during the first two hours is reserved. The cadmium is recovered from the zinc fume, by mixing it with coke breeze, or charcoal as described by C. F. Hollunder, and distilling it fractionally from the mixture. The temp. of the retort is kept at about 800°, so that little more than cadmium oxide is reduced. In this way, a metal over 99·5 per cent. purity is obtained. H Moissan and A. J. P. O'Farrelley distilled the cadmium from its alloy by heating in an electric-arc furnace. H. N. Morse and H. C. Jones heated

cadmium powder in a stream of purified hydrogen for a long time, and then distilled it in vacuo by the process employed by H. N. Morse and W. M. Burton for zinc. The sixth distillate was spectroscopically free from impurities.

Wet methods of extraction have not come into use. They were used at first by F. Stromeyer, J. F. John, and W. Herapath. F. Stromeyer dissolved the cadmiferous zinc in dil. sulphuric acid; precipitated the cadmium sulphide by treatment with hydrogen sulphide; dissolved the washed sulphide in conc. hydrochloric acid; evaporated the soln. to expel the excess of acid; and treated the soln. with ammonium carbonate in slight excess so as to dissolve any copper or zinc which might be present. The washed precipitate was ignited to convert it to cadmium oxide, which was then mixed with carbon and the cadmium distilled from a zinc retort. Another method proposed by G. Jäckel depends on the fact that when cadmiferous zinc fume is treated with hydrochloric acid, the zinc dissolves first and cadmium can be precipitated from its soln. in that acid by metallic zinc. Hence, if cadmiferous zinc fume be treated with insufficient acid to dissolve all the zinc, the excess of zinc will precipitate any cadmium which may have passed into soln. The lead will remain with the cadmium as a residue. The residue is then digested with hydrochloric acid until cadmium begins to dissolve, thus showing that all the zinc has been dissolved. The cadmium is precipitated from a soln. by zinc rods. The mixture of lead and cadmium is then distilled. The soln. of zinc chloride is treated with lime when zinc hydroxide is precipitated.

B. Kosmann treated the zinc dust with a soln. of neutral ammonium carbonate—the zinc dissolved, the cadmium and lead remained as insoluble carbonates. The residue was heated to convert the lead into oxide, and then digested with a soln. of lead acetate, to dissolve the lead oxide. The residual cadmium carbonate was converted into sulphide by dissolving it in dil. sulphuric acid and treating it with hydrogen sulphide; or into oxide by treating it with nitric acid, and subsequent evaporation of the soln., and ignition of the residue. He also extracted the fume first with water, and then with dil. sulphuric acid. The two soln. were mixed and heated to precipitate iron and calcium sulphate; the soln. was diluted and the cadmium precipitated with the arsenic as sulphide. When the mixed sulphide was roasted, the arsenic was volatilized, and cadmium oxide remained.

D. Lance treated the carbonate or oxidized ore with an aq. soln. of an alkylamine alone or in presence of aq. ammonia, and when gradually heated, the zinc is first precipitated as hydroxide, then follows the cadmium hydroxide. W. G. Rumbold and G. Patchin extracted the oxidized ore with an acid soln. of ferric sulphate, and subsequently precipitated the cadmium. O. Unger treated the oxidized ore with a soln. of zinc chloride and precipitated the cadmium by means of metallic zinc. R. Biewend found that metallic cadmium and cadmium alloys, when heated in a glass tube closed at one end, yield a cadmium-mirror, accompanied by a sublimate of cadmium oxide, dark grey when hot, and brown when cold. In the case of zinc ores containing cadmium, potassium oxalate is added as a reducing agent; while calamine, an addition of spathic iron ore, is preferable. From the more volatile sublimates and distillates, that of cadmium can be separated by igniting in a current of air, when the former are volatilized, whilst the latter is converted into cadmium oxide, which is not readily volatile.

H. R. Hanley described a wet process in which the raw material is first obtained in sulphuric acid soln. This is treated with limestone and the precipitated mud—containing copper, cadmium, and zinc—is digested with dil. sulphuric acid, at 60°, and the soln. separated from the cupriferous mud. Cadmium is precipitated on sheet zinc as sponge-cadmium. This is dissolved in an acid cadmium electrolyte. Iron is precipitated with hydrated lime. Thallium, if present, is removed by sodium dichromate in neutral soln. If arsenic is present it is removed by adding ferrous sulphate to the soln., and both iron and arsenic are precipitated together by hydrated lime. The soln. is then acidified, and electrolyzed. The cadmium deposit is finally melted and ingoted.

E. A. Partridge,[18] H. N. Morse and H. C. Jones, and J. E. Bucher purified cadmium by distillation in vacuo up to nine times. W. S. Lorimer and E. F. Smith electrolyzed a soln. of cadmium oxide in potassium cyanide; W. L. Hardin electrolyzed soln. of cadmium chloride or bromide, as did also W. Borchers, P. Denso, A. Brand, F. Mylius and R. Funk, H. N. Morse and H. C. Jones, and R. Lorenz.

G. Bredig,[19] D. Zavrieff, and W. Tichomiroff and A. Lidoff obtained **colloidal zinc** by forming an electric arc with zinc wires under water. T. Svedberg made colloidal zinc and cadmium by connecting a glass condenser of 225 sq. cm. surface with the induction coil and attaching the secondary poles to the electrodes, which are immersed in propyl or isobutyl alcohol contained in a porcelain dish. The zinc was used in a granular form or as wire clippings. When the current is passed, sparks play between the metal particles, and in the course of a few minutes dark-coloured soln. are obtained. These contain no large particles and hence need not be filtered. The isobutyl alcohol is brownish-red in transmitted light and greyish-black in reflected light. G. Bredig also made **colloidal cadmium,** and found that the zinc hydrosol is less stable than the cadmium hydrosol. O. Knoblauch noted Bredig's colloid has photoelectric dispersive powers.

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§ 4. The Physical Properties of Zinc

Zinc is a greyish-white or bluish-white metal, and it is susceptible of a high degree of polish. The cleavage planes on a freshly fractured surface of an ingot of zinc have a brilliant lustre. R. Hennig [1] found the composition of cast zinc to be uniform in a high degree. A. Laurent and C. Holms observed the formation of small rhombic **crystals** of the metal in cracks in the fireclay tubes in which the zinc had been distilled. These rhombic crystals contained four per cent. of iron. C. F. Plattner, W. Kayser, C. W. Zenger, F. Stolba, and J. Nöggerath likewise found long regular six-sided prisms in the walls of drusy cavities. J. Nicklès, and C. W. Zenger obtained pentagonal dodecahedrons by distilling zinc in a stream of hydrogen, but the crystals were not measured. G. H. Williams and W. M. Burton, G. W. A. Kahlbaum, K. Roth and P. Siedler, and P. Termier obtained crystals by distilling the metal in vacuo at a low temp. S. P. Sharples found zinc crystals were developed at the hot junction of a thermoelectric battery. H. N. Warren placed a magnesium rod wrapped in coils of asbestos paper in a soln. of a zinc salt, and found that a zinc-tree was developed. According to G. Bird, if a zinc plate dips in a soln. of sodium chloride contained in a porous pot dipping in a soln. of a zinc salt, in which is fitted a platinum or copper plate, when the circuit is closed, crystals of zinc are formed. R. Lorenz obtained six-sided crystals of zinc by the electrolysis of the molten chloride: while F. Mylius and O. Fromm obtained analogous results. A. Saposhnikoff placed two glass rods in a photographic dish, and arranged a glass plate to which a copper and a zinc wire were fixed to serve as electrodes. The glass plate rested on the glass rods submerged in a soln. of zinc chloride or sulphate. Microscopic crystals of zinc were produced on the glass plate. D. Tommasi, and T. Tommasina electrolyzed water with a zinc plate cathode and a thin wire anode and obtained crystals of zinc. R. Lüpke electrolyzed a conc. soln. of zinc chloride in a **U**-tube fitted with two platinum electrodes. The lower part of the tube was soon filled with dendrites of zinc. W. Holtz obtained a zinc-tree on a small zinc cathode in a soln. of zinc chloride, and connected for electrolysis with a couple of Leclanché cells; and J. Myers electrolyzed a soln. of zinc hydroxide in aq. ammonia with two Bunsen cells. F. Schidlowsky obtained microscopic dentrites by using a zinc anode and a cathode dipping in water. J. Czochralsky compared the **speed of crystallization** of zinc with that of tin and of lead; and G. Tammann and Q. A. Mansuri measured the velocity of crystallization of the compressed powder at different temp. and in different atm.

The rhombohedral crystals of zinc were found by G. H. Williams and W. M. Burton to belong to the hexagonal system with axial the ratio $a : c = 1 : 1{\cdot}3564$. According to G. H. Williams, P. Termier, and G. Linck, zinc and cadmium are isomorphous, and form a eutropic series with magnesium. R. Rieth and F. Beilstein found zinc-sodium alloys, low in sodium, form cubic crystals; and with arsenic

octahedral crystals. J. P. Cooke also found that crystals with 18·82 per cent. of arsenic formed octahedral crystals belonging to the cubic system. The proportion of arsenic in these crystals, added J. P. Cooke, is so much smaller than the amount required to form any probable definite compound, that there can be little doubt that it is present as an impurity, and that the octahedrons are isomorphous mixtures of the two elements. The presence of a certain amount of impurity seems to favour metallic crystallization; and it is possible that it may be the disposing cause in this case, inducing as it were "a monometric condition of the zinc." If arsenic really can make zinc crystallize in the cubic system, then zinc is probably dimorphous. C. W. de la Rue found that when commercial zinc plates are dissolved in a galvanic apparatus, rhombic prisms of a lead-copper-zinc alloy remain. F. H. Storer found that zinc alloys with up to 30 per cent. of copper crystallize in octahedrons belonging to the cubic system.

A. W. Hull found that **X-radiograms** of zinc corresponded with a close-packed hexagonal lattice. They do not fit the hexagonal lattice with the axial ratio 1·356, but require an axial ratio 1·860. The side of the elementary triangular prism is 2·670 A., and the distance between the nearest atoms in the basal plane is 2·670 A., and in the pyramid planes, 2·920 A. The computed density obtained by dividing the mass of the atoms in an elementary cell by the vol. of the cell is 7·04, the observed value is 7·142. L. Hamburger made an ultra-microscopic examination of thin films of zinc. S. Nishikawa and G. Asahara, and M. Ettisch and co-workers studied the effect of rolling and annealing on the X-radiogram of zinc. W. L. Bragg found the atomic diameter to be 2·65 A. The zinc lattice has been studied by M. Polanyi, A. W. Hull and W. P. Davey, etc.

The **fracture** of an ingot of ordinary zinc presents numerous brilliant crystal facets set at various angles, and more or less foliated—in some cases the crystals are in confused masses, in others, the crystal facets are large, even, and distinct. In his paper: *Zur Kenntnis der Moleculareigenschaften des Zinks*, P. A. Bolley showed that the structure of the ingot is modified considerably by the temp. at which the metal is cast. For example, when poured just above the m.p. and allowed to cool slowly, the fracture is finely granular; if heated to redness before pouring, the fracture is more coarsely crystalline; and if heated to a still higher temp., the fracture is coarsely crystalline, and the rate of cooling has but little influence on the crystals. Other things being equal, the slower the cooling the larger the crystals, so that an ingot will appear more coarsely crystalline towards the centre, where the cooling is slowest. According to O. Meyer, and E. H. Schulz and O. Zeller, the fracture of zinc which has been heated to 145°–165° is coarsely crystalline. O. Mügge has studied the **cleavage** of zinc. Zinc which has been crystallized by annealing between 130° and 300° was found by S. Kalischer to lose its ring, and the bending is accompanied by a sound similar to that which occurs with tin.

According to F. Stolba, if zinc be just melted in a crucible and poured on to a non-conducting surface of, say, asbestos, and the liquid portion then run off from that which has solidified, a crust of hexagonal pyramidal crystals will be obtained. Obviously, the external geometrical form of a crystal is developed in a liquid or plastic viscid solid. When a cooling liquid solidifies, the growing crystals interfere with one another, and the resulting solid appears to be a mass of irregular polygons. Most metals are aggregates of crystals grown under these conditions, and when a polished surface is lightly etched, the metal appears to be composed of a number of grains irregular in size and shape; but if deeply etched, the grains themselves also differ in texture. The texture is due to a number of small facets in each grain; the facets are similarly oriented in any one grain so that the general surface of the grain reflects light in a particular direction. Crystallites or incipient crystal forms are common and show as a cross-hatching of the surface. The dendritic zinc crystals were studied by W. Campbell, H. Behrens, etc. The twinning of idiomorphic crystals also appears on etched surfaces.

When the metal is annealed, the crystallitic structure (composed of crystal skeletons) is replaced by a well-defined crystalline structure. According to G. Masing, on heating zinc that has been cold-worked, primary recrystallization of the metal begins immediately throughout the mass without the formation of nuclei. As the temp. rises to 170°–190° nuclei of secondary crystals begin to appear in the mass of primary crystals, and these gradually increase in number and size if the heating is continued slowly until the whole of the metal consists of a mass of large secondary crystals which are coarser the lower the temp. of formation and the longer the heating. If the metal is subjected to a secondary deformation, the secondary crystal nuclei begin to form at 70°. M. Ettisch and co-workers found the crystallites in soft wires are arranged irregularly, and in hard-drawn wires regularly. G. I. Petrenko observed that a polished surface of zinc, cooled slowly from above its m.p. to 180° exhibited large polyhedra (separate or interpenetrating) on which were promiscuously disposed comparatively small ones. The latter were more abundant when the metal was quenched from 360° to 330°, but completely covered the surfaces of the large crystals when the metal was cooled to just below 300°. The phenomenon was reversible, and was regarded as indicating the occurrence of an allotropic transformation between 290° and 300°. K. E. Bingham studied the microstructure of zinc quenched in the ranges of temp. supposed to belong to assumed α-, β-, and γ-forms of zinc—and found that this hypothesis fits her observations. D. H. Ingalls studied the relation between the mechanical properties and the microstructure.

G. Timofeeff showed that zinc which has been squeezed in a vice appears homogeneous, and under the microscope no crystals are discernible; G. T. Beilby also showed that the polished surface of the crystalline metal is covered by an amorphous glass-like film which can be removed by a suitable etching liquid, so as to expose the subjacent crystalline structure. When the non-crystalline metal is annealed, recrystallization sets in. S. Kalischer observed that recrystallization begins at about 150°. According to G. Tammann, large crystals of zinc appear at 75°, and their size increases as the temp. rises to 250°, and increases again when reheated to 350°; Z. Jeffries and R. S. Archer state that the lowest temp. at which the recrystallization of cold-worked zinc has been observed is the room temp. F. Novak found that, within certain limits, the higher the annealing temp. of zinc, the more rapid the crystallization. At any given temp., the size of the crystal grains is limited by the duration of heating. H. Behrens found recrystallization is completed at 200°. The large individual crystals of cast zinc become striated under a slight shock. J. A. Ewing and W. Rosenhain found commercial sheet zinc has no large crystals, but is tough, and when heated to 200° for half an hour, it is crystalline, brittle, and, when bent, breaks along definite cleavage planes, and emits a " cry " like tin. They also found that when the metal is strained beyond its elastic limit, the surface of each crystalline grain becomes marked by one or more systems of lines generally running straight and parallel. The lines or slip-bands are slips along cleavage or gilding planes in the crystal. The directions of the lines change from grain to grain. The lines become more and more numerous and emphatic, the greater the strain. A. Lacroix found the **percussion figure** of zinc shows lines parallel to the sides of the hexagon. H. Behrens, and J. A. Ewing and W. Rosenhain have studied the twinning of zinc crystals. According to E. Cohen and K. Inouye, when a strip of zinc with a cross etched on its surface by an acid is kept in contact with another unetched strip of zinc by press. at 100°–180° for 17–48 hrs., a similar cross will be developed on the second strip. This does not occur at ordinary temp.

For **etching zinc or cadmium** surfaces, G. Timofeeff used a few drops of a mixture of 94 per cent. nitric acid and 6 per cent. chromic acid, added to 50 or 100 c.c. of water; G. H. Gulliver recommended a soln. of one part of iodine, 3 parts of potassium iodide, and 10 parts of water. J. Czochralsky recommended a highly conc. soln. of chromic acid. G. Cartaud used a soln. of picric acid in acetone; S. Kalischer used sulphuric acid with a little nitric acid, or a soln. of cupric sulphate. Five to ten per cent. soln. of alkali hydroxide are often used. H. H. Hayes recommended nitric acid of sp. gr. 1·5.

If over 0·1 per cent. of iron is present, distinct crystallites are produced which are considered to be the cause of the light specks on the crystal faces of a fractured ingot of zinc. If the zinc contains lead, the latter is rejected by the freezing zinc, and forms minute globules often occupying the cleavage cracks caused by the contraction of the crystalline zinc during solidification. If zinc oxide be present, it often collects at the crystal boundaries, making them appear thick. G. Cartaud has studied the effect of 0·5 per cent. additions of silver, lead, copper, bismuth, cadmium, tin, arsenic, antimony, iron, aluminium, manganese, nickel, and phosphorus on the metal. E A. Lewis, E. H. Schulz and R. Melaun, and F. Novak also studied the effect of impurities on the crystal structure of zinc.

The reported values for the **specific gravity** of zinc vary from R. Schiff's [2] 6·966 at 12° to P. A. Bolley's and W. C. Roberts-Austen and J. Wrightson's 7·20. The best representative value is 7·142. G. W. A. Kahlbaum and co-workers found the sp. gr. of distilled zinc to be 6·9225 at 20°/4°, and after compression up to 10,000 atm., 7·12722. According to W. Spring, the sp. gr. of zinc is 7·142 at 16°, and after compression for three weeks at 20,000 atm., 7·153, and after a repetition of the treatment, 7·150. C. J. B. Karsten found the sp. gr. of rolled commercial zinc is 7·1908, and after hammering and rolling the sp. gr. may reach 7·2 or 7·3. According to S. Kalischer, the sp. gr. of ordinary zinc at 0° is 7·1812, and when crystallized, 7·1841. P. A. Bolley proved that there is no variation in the sp. gr. of zinc at a given temp. before and after fusion ; any variation which may have been observed is entirely due to the development of minute cavities in the metal ; so that a piece of zinc weighed whole has a lower apparent sp. gr. than when it is fractured into smaller pieces. A. Matthiessen found that the sp. gr. of redistilled arsenic-free zinc is 7·144 at 15·5° ; after fusion 7·150 at 14·4° ; and after another fusion 7·149 at 15°. The original piece before distillation had a sp. gr. 7·148 at 15°. P. A. Bolley found the sp. gr. is lower when the metal is cast at a high than when cast at a low temp. Thus, when poured near its m.p. the sp. gr. zinc is 7·178 when rapidly cooled, and 7·145 when slowly cooled ; while when poured almost at a red heat, the sp. gr. was 7·109 if rapidly cooled, and 7·120 if slowly cooled. C. F. Rammelsberg on the contrary found that the sp. gr. of cast zinc is dependent neither on the temp. of pouring nor on the mode of cooling ; he obtained between 7·10 and 7·16 for the slowly cooled cast metal, and between 7·04 and 7·14 for the rapidly cooled metal. K. E. Bingham slowly cooled a piece of rolled zinc, and heated portions to different temp. for 30 mins. The samples were then quenched. Samples heated to 50° had a sp. gr. 7·080 ; to 100°, 7·086 ; and to 150°, 7·089. There was an abrupt rise in sp. gr. to 7·16 for samples heated to 150° and higher temp. as indicated in Fig. 6.

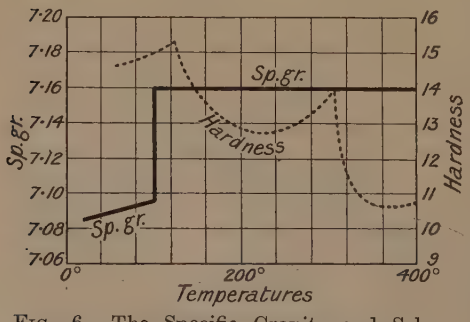

Fig. 6.—The Specific Gravity and Scleroscopic Hardness of Zinc annealed at different Temperatures.

T. M. Lowry and R. G. Parker found that as with most metals the sp. gr. of zinc is reduced by working. Thus, the sp. gr. of purified zinc was 7·1374, and that of the filings from the same metal 7·1323. When completely annealed, the worked metal contracts, but when partially annealed there is an expansion. The sp. gr. of zinc was found by W. C. Roberts-Austen to change from 7·2 to 6·51 when melted ; this corresponds with a contraction during solidification. C. M. Marx, and F. Nies and A. Winkelmann noted the contraction of molten zinc in the act of solidification. According to M. Töpler, a gram of zinc expands 0·010 c.c. in passing from the solid to the liquid state. L. Playfair and J. P. Joule gave 6·512 for the sp. gr. of melted zinc ; G. Quincke gave 6·9. T. R. Hogness gave $D=6·59-0·00097(\theta-419)$ for the sp. gr.

of molten zinc at $\theta°$. P. Pascal and J. Jouniaux found the sp. gr. of liquid zinc in an inert gas at the m.p. 418° to be 6·92; at 600°, 6·81; and at 800°, 6·57. According to W. T. Cooke, the **vapour density** of zinc in an atm. of nitrogen is 32·5 (hydrogen unity); in an atm. of argon, 36·4; in an atm. of hydrogen, 36·4; and in an atm. of helium, 35·8. According to V. Meyer and J. Mensching's measurements, the vap. density of zinc vapour 2·36 (air unity) corresponds with a monatomic molecule.

E. Donath and J. Mayrhofer have studied the **atomic volume** of zinc. W. Thomson, and G. Jäger made estimates of the **molecular diameter.** The former deduced that "plates of zinc and copper so thin as 4×10^{-8} cms., and placed as short a distance as 4×10^{-8} cms. from one another, form a mixture closely approaching to a molecular combination, if indeed plates so thin could be made without splitting atoms." W. L. Bragg gave $0·132\mu\mu$ for the at. radius of the at. spheres; M. N. Saha, 0·077. K. F. Slotte gave $6·3\times10^{-9}$ cms., for the edge of the molecule assumed to be a cube. C. T. Heycock and F. H. Neville determined the **molecular weight** of zinc dissolved in cadmium, tin, lead, and bismuth.

According to E. Cohen,[3] when zinc of sp. gr. 7·129 is heated in the presence of a sat. soln. of zinc sulphate for 33 hrs. at 100°, its sp. gr. falls to 7·102; hence, it was inferred that ordinary zinc is in a metastable condition and that the allotropic modification formed at the higher temp. passes slowly at ordinary temp. into a stable variety having a sp. gr. 6·92. There are indications that the transition temp. is near 64·9°.

Ordinary zinc is a comparatively soft metal, though much harder than tin and silver, and it clogs a file; but when pure, zinc is softer than silver. According to C. Margot,[4] if glass is quite dry, it can be scratched by zinc. According to F. C. Calvert and R. Johnson, if the **hardness** of cast iron be 1000, that of zinc is 183. A. Kürth gave 46·0, C. A. Edwards 45·5, for the hardness of zinc on Brinell's scale. The Brinell's hardness of cast zinc is 38·1, copper 40·0, and silver 24·8. Purified zinc is appreciably hardened by quenching in water after casting. According to T. K. Rose, zinc is hardened by mechanical treatment—*e.g.* rolling—and requires annealing for half an hour at 125°. Zinc hardened by rolling is in an unstable condition at ordinary temp., and gradually changes to the soft state. Thus, the scleroscope hardness of a sample of rolled zinc was 36·0, and after 97 days the hardness had fallen to 31·0. K. E. Bingham measured the hardness of zinc heated to different temp. for 30 mins. and then suddenly quenched. The Brinell's hardness tests were somewhat erratic, but the scleroscopic tests are represented by dotted curve, Fig. 6. There are critical points at 160° and 330°. P. Ludwik found the curve representing the variation of hardness with temp. is continuous, and slightly convex towards the temp. curves, whether the metal has been slowly or rapidly cooled. The hardness of zinc is usually raised by the presence of impurities: thus E. A. Lewis found the hardness of zinc is raised by phosphorus; C. Karmarsh found a similar result with 0·1 per cent. of iron and 0·5 per cent. of copper; while F. Novak found 0·25 per cent. of cadmium makes zinc harder, and over 0·5 per cent. makes the zinc softer. J. R. Rydberg, P. Ludwik, A. Kürth, and S. Bottone have also made measurements of the hardness of zinc. J. Okubo found the scleroscopic hardness of zinc to be 10·8 when that of lead is 1·35; he also measured the **coefficient of restitution** on impact.

K. Iokibe and S. Sakai [5] found the coeff. of **viscosity** of zinc to be $410·7\times10^8$ at 22°. K. Honda and S. Konno gave $27·4\times10^8$ at 20° for the coeff. of normal viscosity of rolled zinc; and $9·27\times10^8$ for the metal annealed at 200°. Measurements were also made by C. E. Guye and co-workers. G. Quincke found the **surface tension** of zinc in air at 360° to be 967·4 dynes per cm., and the **capillary constant** a^2=28·6 sq. mm.; the corresponding numbers in carbon dioxide are 103·7 and 30·6 respectively. Between 580° and 630°, the surface tension of zinc is 707·5 dynes per cm., and the capillary constant 25·54 sq. mm. S. W. Smith gave 707·5 dynes per cm. for the surface tension of zinc at 580°–630°, and a^2=24·8. T. R. Hogness gave $\sigma=758-0·090(\theta-419)$ for the surface tension of molten zinc at $\theta°$. I. Traube

gave 108,900 megabars or 10^6 dynes per sq. cm. for the **internal pressure** of solid zinc. G. Meyer gave for the **diffusion coefficient** of zinc in mercury, in sq. cm. per day, $k=2{\cdot}09$ at 15°; and M. von Wogau, $k=2{\cdot}18$ at 11·5°, and $k=2{\cdot}90$ at 99·2°. The diffusion of copper into molten zinc was studied by O. F. Hudson, and H. Weiss. According to A. Masson, the **velocity of sound** in zinc is 3698·5 metres per sec. when the velocity in air is 332 metres per sec.; G. G. Gerosa gave 3680·9 metres per sec. for the velocity of sound in zinc at 13°. S. Kalischer found that rolled zinc loses its sonorous ring when heated, and the ring then becomes as dull as lead—the higher the temp. the duller the sound.

According to H. Behrens,[6] highly purified zinc is malleable and may be rolled into sheets at ordinary temp., but the commercial metal is then moderately hard and brittle. The **malleability** of commercial zinc lies between that of lead and of iron, and the **ductility** between that of copper and of tin. An ingot or cake of commercial zinc can be easily broken to pieces under the hammer. The malleability of zinc is very much greater than that of bismuth or antimony. The elongation in the tensile strength test can be regarded as a measure of ductility—Fig. 7. H. F. Moore found that sheet zinc is more ductile with the grain than across the grain (*i.e.* perpendicular to the direction of rolling) and that the ductility of zinc is less than that of mild steel. According to W. Campbell, if hammered or rolled cold, the crystalline structure is broken up and the metal splits and breaks up. Above 205°, zinc is so brittle that it may be readily pulverized by trituration in an iron mortar. According to A. F. de Fourcroy, the fact that zinc can be pulverized in a mortar when warmed to a temp. below its m.p. was known to P. J. Macquer in 1801. In 1805, C. Hobson and C. Sylvester made the important discovery that commercial zinc, between 100° and 150°, becomes malleable and ductile, and they obtained a patent for "a method of manufacturing the metal called zinc into wire and into vessels," for zinc can then be rolled into sheets and drawn into wire, and, after cooling, these properties are to some extent retained. E. H. Schulz and R. Fiedler found samples of zinc with the notched bar impact test gave results varying from 0·55 to 0·75 kgrm. metres per sq. cm. The **resistance to impact** decreased with fall of temp.

E. Prost and A. van de Casteele found that the ductility of zinc is appreciably lowered by 0·25 per cent. of cadmium; 0·02 per cent. of arsenic makes zinc harder and more brittle; antimony acts like arsenic, but is not so harmful; 0·01 per cent. of tin is objectionable; copper does not harden zinc if less than 0·08 per cent. is present, but the zinc cannot be rolled if 0·19 per cent. is present; 0·12 per cent. of iron is permissible; and 1·0 to 1·25 per cent. of lead does not interfere with rolling, but a slight increase affects the malleability—the excess of lead remains unalloyed, and forms patches on the sheet.

It has been suggested that the phenomenon near 170° is possibly due to the transformation of zinc from one allotropic form to another. Besides E. Cohen's two **allotropic forms** of zinc (*vide supra*) with a transition about 64·9°, there is a third form with a transition about 170°, and a fourth with a transition at about 310°. These two latter transition points are in agreement with observations on the electrical resistance, electrolytic potential, sp. gr., hardness, mechanical properties, and microstructure. M. P. Lastschenko found a change in the sp. ht. curve of zinc in the vicinity of 340°–350°, which he interpreted as corresponding with an allotropic change in the nature of the metal. The heat of transformation is estimated to be 190 cals. per gram-atom of zinc. Neglecting E. Cohen and W. D. Heldermann's transition point, C. Benedicks assumed that zinc is trimorphous, with enantiotropic transition points:

$$\alpha\text{-Zn} \overset{170^\circ}{\rightleftharpoons} \beta\text{-Zn} \overset{310^\circ}{\rightleftharpoons} \gamma\text{-Zn}$$

P. A. Bolley stated that zinc which has been cast at a low temp. is more readily attacked by acids than the metal cast at a red heat; and K. E. Bingham found that zinc quenched from the range of temp. of γ-zinc is more difficult to etch than zinc quenched from the ranges of the β- or α-forms. As previously indicated, C. Benedicks and R. Arpi stated that previous observations on the discontinuity in the

electrical resistance of zinc between 170° and 350° is due to the presence of cadmium or lead as impurities, but K. E. Bingham regards this as an improbable explanation. For criticisms *vide* allotropic copper.

According to C. Mentzel, the malleability of zinc depends to some extent on the temp. at which it has been melted, for it is more malleable if poured near its m.p. than if cast at a higher temp. A. Martens found the malleability to decrease rapidly as the temp. rises above 150° ; and, according to H. le Chatelier, the malleability or ductility changes with temp., thus :

	15°	70°	150°	200°	250°	300°
Elongation . . .	16·5	300	500	40	3	2 per cent.
Breaking load . .	12·4	3·6	2·4	0·9	0·7	0·6 kgrm. per sq. mm.

Zinc is hardened by rolling or mechanical treatment generally, but the hardness can be removed by annealing as previously indicated, soft sheet zinc becomes brittle after it has been heated to a temp. bordering on its m.p. Impurities in the metal have a marked influence on the malleability of zinc. Thus, C. Karmarsch found that zinc with 3 per cent. of lead may be rolled, but if one per cent. of tin is present, the zinc cracks at the edges during the rolling. F. Novak found that zinc is rendered less brittle if it contains 0·25 per cent. of cadmium, and more brittle if it contains over 0·5 per cent. of cadmium. According to C. Künzel, zinc with 0·2 to 0·3 per cent. of chlorine cannot be rolled. According to E. Prost and A. van de Casteele (1913), if the amount of lead in the zinc exceeds 1·25 per cent. the malleability is reduced, the limit with cadmium is 0·25 per cent. ; while if over 0·02 per cent. of tin, arsenic, and antimony is present, the zinc is hardened, and this additively.

H. Buff[7] found the **modulus of elasticity** or **Young's modulus** to be 10,800 to 11,900 kgrms. per sq. mm. ; and for cast rods of metal containing 0·1 per cent. each of lead, cadmium, and iron, E. Grüneisen found 12,370 to 13,100 kgrms. per sq. mm., while for impure zinc, with 1·1 per cent. of lead, 0·25 per cent. of copper, and 0·03 per cent. each of iron and cadmium, he found 8910 kgrms. per sq. mm. W. Voigt gave 10,300, and J. Kiewiet 10,477 kgrms. per sq. mm. ; G. Wertheim, 8734 kgrms. per sq. mm. at 15° for cast zinc ; C. Schäfer gave 4296 kgrms. per sq. mm. at 20°. O. Meyer found the modulus of elasticity of rolled zinc plate 0·044 to 0·051 in. thick, is $12{\cdot}85\times10^6$ lbs. per sq. in. with the grain, $14{\cdot}50\times10^6$ across the grain, or an average of $13{\cdot}62\times10^6$ lbs. per sq. in. For annealed zinc, he obtained $15{\cdot}95\times10^6$ lbs. per sq. in. W. Sutherland gave the elastic modulus of zinc between 7670 and 10,550, or an average 9300 kgrms. per sq. mm. ; and he estimated that the elastic modulus is 9300 kgrms. per sq. mm. at 15° ; and 1490 kgrms. per sq. mm. at −273°. H. Mark and co-workers studied the mechanism of the stretching of zinc.

For the **torsion modulus,** *rigidity,* or *shear modulus,* J. Kiewiet gave 3820, W. Voigt 3880, and C. Schäfer 1614·4 kgrms. per sq. mm. at 20°. N. Katzenelsohn found 40·0 per cent. change in the torsion modulus between 0° and 100°, and C. Schäfer, 48·37 per cent. change between −186° and 20°. W. Sutherland gave for the ratios of the rigidity at 100° to the value at zero 0·749, and H. Tomlinson, 0·843. For the absolute values of the rigidity between 0° and 20° in grams per sq. cm. Lord Kelvin (W. Thomson) gave 360×10^6, H. Tomlinson 340×10^6, and J. Kiewiet 380×10^6. W. Sutherland's mean is 350×10^6, or 350×10^6 grms. per sq. cm. at 15°, and at absolute zero 426×10^6 grms. per sq. cm. H. Tomlinson represented the rigidity of zinc at $\theta°$ by $nt=n_0(1-0{\cdot}00108\theta-0{\cdot}0000049\theta^2)$. W. Sutherland gives $n/N=1-(\theta/T)^2$, where n denotes the rigidity at $\theta°$; N, the value at absolute zero ; and T, the absolute m.p.

P. Berthier noted that zinc wire 0·002 metre in diameter breaks under a load of 12 kgrms. J. Bauschinger found with tests lasting 6 mins. the average **tensile strength** of rolled zinc is 29,100 lbs. per sq. in., and with tests lasting 81 mins., 23,300 lbs. per sq. in. Hence the rapidity of testing increases the tensile strength of rolled zinc, but with cast zinc the influence of rapidity of loading is slight. A. Martens

found for the ultimate tensile strength, in lbs. per sq. in., and the percentage elongation after rupture :

	19°–27°	80°	120°	150°	170°	200°
Tensile strength . .	20600	12500	8960	5790	7960	6120
Elongation . . .	12·4	29·4	59·4	101·5	17·1	7·2

The tensile strength is low, and the ductility is a maximum, at about 150°, and hence this is the most favourable temp. for rolling. H. le Chatelier, and P. Ludwik made some observations on the effect of temp. on the breaking stress of zinc. J. Dewar found the breaking stress of cast zinc rods, 0·2 in. diameter, at 15° and −182° to be respectively 25 and 26 lbs. per sq. in. O. Meyer also found the results indicated in Table II, where the data are expressed in lbs. per sq. in. for plates

Table II.—Tensile Strength Tests of Rolled Zinc.

	Rolled.			Annealed.
	With grain.	Across grain.	Average.	Average.
Stress at 1st permanent set .	1,990	2,420	2,130	2,480
Stress at limit of proportionality of stress to deformation .	710	1,280	995	1,710
Yield point	11,400	13,640	12,500	11,100
Ultimate tensile strength .	30,400	36,800	33,600	17,500
Elongation per cent. . .	27·2	9·7	18·5	4·6
Reduction of area . . .	43	17	30	5
Modulus of elasticity . .	12,850,000	14,500,000	13,620,000	15,950,000

0·044 to 0·051 in. thick. Specimens cut across the grain, *i.e.* perpendicular to the direction of rolling, are rather stronger and stiffer than when cut with the grain, *i.e.* parallel to the direction of rolling. The stresses at the elastic limit and yield point are very low, and the yield point is not sharply marked, for the flow of the metal at a high stress goes on for a long time. A ten minutes' immersion of the plates in 5 per cent. nitric acid did not appreciably lessen their ductility or strength. H. F. Moore found that zinc either rolled or cast has no well-defined yield point and its elastic limit is very low. Zinc possesses a relatively high degree of plasticity. The ultimate tensile strength of thin rolled zinc plate (not more than 0·05 in. thick) is about 24,000 lbs. per sq. in. The modulus of elasticity of zinc in tension is about 13×10^6 lbs. per sq. in. The stress per square inch of area sheared developed in punching or shearing rolled zinc plates is about 40 per cent. of the stress developed in punching or shearing mild steel plates. The energy per square inch of area sheared per inch thickness of plate required to punch or shear rolled zinc plates is about 30 per cent. of the energy required to punch or shear mild steel plates. K. E. Bingham measured the tensile strength—maximum stress in tons per sq. in.—and percentage elongation on 2 in. Observations made on the metal at different temp. also showed critical points in the maximum stress at about 190° and 300° ; and in the percentage elongation between 160° and 180°, and at about 300°. The tensile strength tests are shown by the continuous curve, Fig. 7 ; and the percentage elongations by the dotted curve in the same diagram. The critical points appear as breaks in the curve. Experiments were also made on test pieces which had been annealed at different temp. and then quenched, and they too showed critical points in the curve of maximum stress for zinc quenched at 180°, and for zinc quenched between 300° and 310°. The percentage elongations gave critical points at the same temp. E. H. Schulz and co-workers have made observations on this subject. O. Meyer, and F. Novak examined the effect of cadmium and lead on the tensile strength of zinc, and found that 0·25 per cent. raises, and over 0·5 per cent. depresses, the tensile strength of zinc. 1·5 per cent. of lead and arsenic, antimony, and tin

make zinc brittle. E. Grüneisen's and A. Mallock's values for **Poisson's ratio** for zinc are 0·2 to 0·3, *i.e.* the ratio of the transverse contraction to the longitudinal extension under tensile stress. B. MacNutt and A. Concilio discussed the noises which occur when zinc is stressed above certain loads.

T. W. Richards and co-workers found the average **compressibility,** that is, the fractional change of vol. caused by one megabar press., between 100 and 500 megabars,

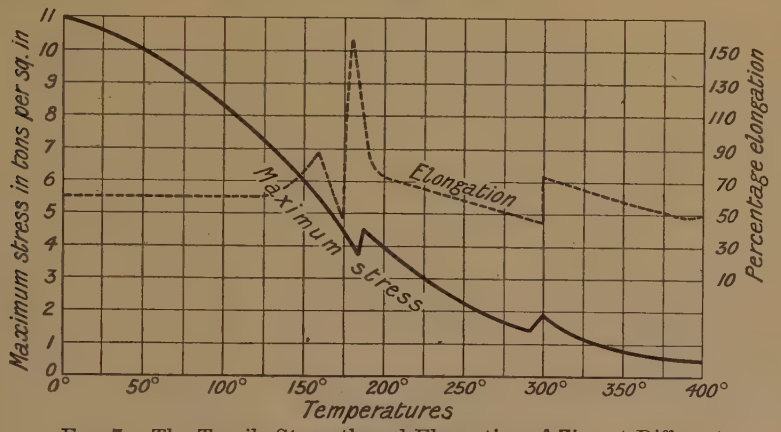

FIG. 7.—The Tensile Strength and Elongation of Zinc at Different Temperatures.

to be $1{\cdot}5\times10^{-6}$ per unit vol. per megabar, or $13{\cdot}70\times10^{-8}$ per at. vol. per megabar. W. Voigt gave 0·9 to $1{\cdot}5\times10^{-6}$ for the compressibility of zinc. S. Lussana found that a change of temp. had but a small effect on the coeff. of compressibility which was $2{\cdot}70\times10^{-6}$ at 9°; $2{\cdot}77\times10^{-6}$ at 105°; $2{\cdot}81\times10^{-6}$ at 156°; and $2{\cdot}83\times10^{-6}$ at 170°. The vol. of zinc at 0° is estimated to change 0·0200 with a change of press. from 0 to 12,000 kgrms. per sq. cm. L. H. Adams, E. D. Williamson and J. Johnston gave $1{\cdot}74\times10^{-6}$ per megabar for the compressibility of zinc at zero press. and $1{\cdot}43\times10^{-6}$ at 10,000 megabars press. They represented the change in vol., δv per c.c. produced when the press. changes from p_0 to p, by $\delta v=0{\cdot}20\times10^{-4}+1{\cdot}677\times10^{-6}(p-p_0)+1{\cdot}52(p-p_0)^2$. What N. S. Kurnakoff and S. F. Schemtschuschny call the **plasticity,** *i.e.* the press. required to produce a flow of the metal through a given opening at ordinary temp. is 75 kgrms. per sq. mm. N. Werigin, S. Lewkojeff, and G. Tammann also measured the velocity of flow by pressing warm zinc and other metals through an opening. W. E. Dalby studied the plastic extension of zinc. When zinc is compressed by 300 atm., C. J. Burton and W. Marshall found a rise of temp. of 0·062°; and when zinc is suddenly subjected to 388 atm. press., the observed rise is 0·00016° per atm. increase of press. E. Jänecke made some press. measurements on zinc, and concluded that a transformation occurs between 104° and 120°. The same method gave far too low a point for the m.p. of tin, so that these observations are not suitable for measuring the transformation points of a metal.

P. Berthier's value [8] for the **coefficient of linear expansion** of zinc between 0° and 100° is 0·000029412; H. Fizeau's value at 40° is 0·00002918, and at 50°, 0·00002908; and A. Schulze's value is 0·0000364 between 20° and 100°. A. Matthiessen's value between 0° and 100° is 0·00002976, and he found unit vol. at 0° becomes at θ°, $1+0{\cdot}000082222\theta+0{\cdot}000000070\theta^2$. C. Schäfer's value for the coeff. of expansion is 0·00002905, and W. Voigt gave 0·0000251. N. E. Dorsey found 0·00001910 at −170°, and 0·000002970 at 10°; E. Grüneisen obtained $0{\cdot}0_41006$ between −183° and 13°; and $0{\cdot}0_41711$ between 19° and 100°. H. Kopp and A. Matthiessen found 0·000089 per degree for the cubical expansion between 0° and 100°. C. B. Comstock found variable results for the expansion of zinc at the same temp. E. Heinemann found that when a zinc rod has been heated for a long time,

it does not return to its original size on cooling. F. C. Calvert and R. Johnson measured the thermal expansion of zinc; they also found that if the **thermal conductivity** of silver is 100, the conductivity of a vertically cast zinc rod is 62·8; of a horizontally cast rod, 60·8; and of rolled zinc, 64·1. G. Wiedemann,[9] however, found that if the thermal conductivity of silver is 100, that of zinc is 19. F. A. Schulze stated that the conductivities of zinc, cadmium, lead, and tin are of the same order. F. E. Neumann gave the conductivity of tin as 362 when that of copper is 130·6. G. Kirchhoff and G. Hansemann found at 15°, the absolute value of the conductivity of zinc is 0·2545 cal. per cm. per sq. cm. per sec. per degree. H. F. Weber obtained the high value 0·3056; A. Berget, 0·303 between 0° and 30°; and L. Holborn and W. Wien, 0·292. W. Jäger and H. Diesselhorst found 0·2653 at 18°, and 0·2619 at 100°; and C. H. Lees gave 0·280 at —170°, and 0·268 at 18°. G. Glage obtained 0·274 for the absolute thermal conductivity at 50°, and 0·412 for the temp. conductivity, *i.e.* λ/Ds, where λ represents the thermal conductivity, D the density, and s, the sp. ht. W. Jäger and H. Diesselhorst gave 0·4066 for the temp. conductivity at 18° and 0·3914 at 100°, with the temp. coeff. of —0·45 per cent. S. Konno found the thermal conductivity of solid zinc fell from 0·263 at 18° to 0·220 at the m.p.; and on melting the conductivity of the liquid fell to 0·140 at 400°, and to 0·137 at 578°, as illustrated in Fig. 8. P. W. Bridgman found the thermal conductivity of zinc increases linearly with press.

H. Kopp [10] found the **specific heat** of zinc to be 0·0932 between 19° and 47°; P. L. Dulong and A. T. Petit, 0·0927 between 0° and 100°; H. V. Regnault, 0·0956 between 0° and 20°; L. Schütz, 0·0963 between 0° and 100°; A. Schüler and W. Wartha, 0·09393; H. Tomlinson, 0·0983; W. Gaede, 0·09356 between 0° and 100°; A. Naccari, 0·0951 at 100°; G. W. A. Kahlbaum, K. Roth, and P. Siedler, 0·0939 for distilled zinc, and 0·0940 for the same zinc which had been compressed at 10,000 atm.; U. J. J. le Verrier, 0·096 between 0° and 110°, and a very variable result, approximately 0·105, between 110° and 300°; and 0·122 between 300° and 400°, and it increases rapidly over 400°. P. Schübel gave 0·0934 at 100°; 0·09644 at 200°; 0·0976 at 300°; and 0·09924 at 396°. E. Bède represented his observations at $\theta°$ by $0·0865+0·000064\theta$; and A. Naccari, by $0·0907+0·00004440\theta$. F. Glaser obtained for highly purified solid zinc at 374°, 0·099925, and at 430° when melted, 0·175992; for zinc with 1·29 per cent. of lead, and 0·60 per cent. of iron, the sp. ht. at 281·5° was 0·099566, and at 488°, 0·18113. U. Behn found the sp. ht. at —186° to be 0·0727; and H. E. Schmitz found 0·0836 for purified zinc at —185°, and 0·0931 at 60°; and respectively 0·083 and 0·091 for the less pure metal. For the sp. ht., and for the at. ht., C_p, E. H. and E. Griffiths found the following data above —127·5°, and F. Pollitzer the numbers below that temp.:

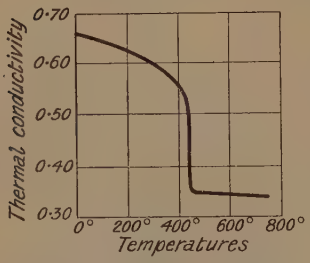

FIG. 8.—Thermal Conductivity of Liquid and Solid Zinc.

	—206°	—179°	—127·5°	—61·9°	0·1°	21·6°	50·6°	97·5°	123·5°
Sp. ht. . .	0·0523	0·0696	0·08421	0·08898	0·09176	0·09265	0·09412	0·09521	0·09570
At. ht. . .	3·42	4·55	5·50	5·82	6·00	6·06	6·15	6·22	6·26

J. Dewar found 0·0384 for the sp. ht. of zinc at the temp. of liquid air, and the corresponding at. ht. 2·52. J. W. Richards represented the sp. ht. of zinc at $\theta°$ between 0° and 400° by $0·0906+000044\theta$; and he estimated that the sp. ht. of the vapour is 0·325 Cal. per cub. metre, or 0·076 Cal. per kgrm. I. Itaka found the sp. ht. of zinc undergoes a discontinuous change during melting, being, at the m.p., 0·110 for the solid, and 0·121 for the liquid; the corresponding at. ht. are 7·20 and 7·91. As indicated above, P. N. Laschtschenko claimed to have obtained a critical point between 340° and 350° in his calorimetric observations on zinc. K. E. Bingham

found no critical points on the **heating curves** of zinc between 25° and 390°. R. C. Tolman gave 39·7 for the **entropy** of zinc at 25°; G. N. Lewis and co-workers obtained 38·17 (gas), and 9·83 (solid).

An early observation of J. Black [11] gave 260° for the **melting point** of zinc; L. B. G. de Morveau, 374°; J. F. Daniell, 412°; and G. G. Person, 433·3° and 415·3° respectively with mercury and air thermometers. Among the later observers, H. L. Callendar and E. H. Griffiths gave 417·57°; G. W. A. Kahlbaum gave 424°; and F. Wüst and co-workers, 419°. The majority of modern observers—L. Holborn and A. L. Day, G. Hindrichs, L. Donsky, E. H. Griffiths, J. Petrenko, A. von Vegesack, K. Lewkonja, A. C. Egerton, V. Meyer, H. L. Callendar, C. Schäfer, etc.—have given numbers very close to 419·4°, which K. Scheel, L. I. Dana and P. D. Foote, and W. Guertler and M. Pirani consider may be taken as the best representative value. C. T. Heycock and F. H. Neville found the f.p. is depressed by cadmium, aluminium, tin, and bismuth; while it is raised by copper, silver, and gold. C. Margot found molten zinc sticks to glass. A. O. Ashman recommended zinc, f.p. 419°, as a fixed point in the calibration of pyrometers because the f.p. on the cooling curve is very sharp; there is no undercooling; the metal is very little oxidized at this temp., and the oxide is not soluble in the metal and therefore has no influence on the f.p. F. Glaser gave 29·86 Cals. for the latent **heat of fusion**; D. Mazzotto, 28·1; and G. G. Person, 29·13 Cals. per kgrm., or 1·8 Cals. per gram-atom. V. Czepinsky gave 1·93 Cals. per gram-atom. C. T. Heycock and F. H. Neville gave 1·82 Cals. per gram-atom. A. C. Egerton, U. J. J. le Verrier, and A. Ledebur have made observations on this subject.

E. Tiede and E. Birnbräuer [12] found that when zinc is heated in the vacuum furnace, it forms a crystalline sublimate on a hot surface, and a mirror on a cold surface. C. Barus, and O. Ruff and B. Bergdahl measured the **vapour pressure** of zinc in mm. of mercury and the temp. of distillation under two atm. press., and the former found:

	675°	699°	732°	758°	792°	833°	873°	900°	933°
Vap. press. . . .	26	35	65	101	158	264	425	557	768

J. W. Richards also calculated the following values for the vap. press. of zinc in mm. of mercury:

	248°	363°	477°	592°	706°	821°	930°	1298°	1928°
Vap. press. . . .	0·0002	0·026	0·779	9·23	58·82	242	760	10488	123120

The vap. press. curves for zinc, cadmium, and mercury are indicated in Fig. 9. A. C. Egerton has made observations on the vap. press. p, of zinc, and at the absolute temp. $T°$ he found $p=1·17\times10^{14}T^{-\frac{1}{2}}e^{-3·28\times10^4/RT}$ dynes per sq. cm., or, $\log p=10·9443-0·5 \log T-7176T^{-1}$ in mm. The slope of the vap. press. curve of zinc at the m.p. is $4·41\times10^{-3}$; the vap. press. formula of J. A. M. van Liempt is $p=-684/T+5·70$ atm., where T is the absolute temp.; the sublimation curve is $\log p=-7266/T+6·28$. C. Barus' formula is $\log p=20·98-8619T^{-1}-3·868 \log T$; and H. Braune's $\log p=6655T^{-1}-1·147 \log T+12·046$. H. C. Greenwood also made some measurements of the vap. press. of zinc; the latter found $6·3\times760$ mm. at 1393°, $11·7\times760$ mm. at 1503°; $21·5\times760$ mm. at 1553°; and 53×760 mm. at 1783°. F. A. Henglein gave $\log p=-4·6222\times(1179·6T^{-1})^{1·1092}$ atm. J. A. M. van Liempt

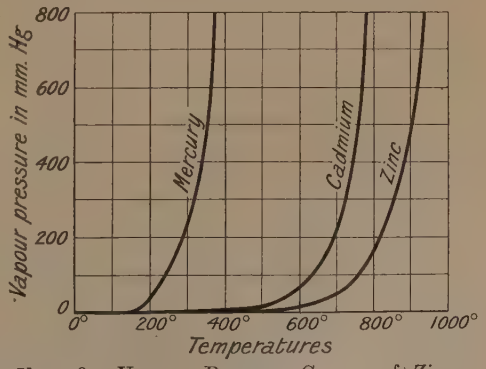

FIG. 9.—Vapour Pressure Curves of Zinc, Cadmium, and Mercury.

gave 26·10 for **Trouton's constant**; H. Braune, 7·24 for the **chemical constant.** C. Zenghelis inferred that zinc evaporates at ordinary temp. in a dry space because it formed a gold-coloured alloy with silver foil placed a short distance away; W. Spring also inferred that zinc is volatile at 300° because it then forms an alloy with lead; and it alloys with copper at 380°; C. J. Hansen, E. Demarçay, A. Schuller, and F. Krafft said that zinc evaporates in vacuo at 184°, and it sublimes rapidly in vacuo when exposed to green cathode rays. J. Stark and S. Kinoshita made zinc-vapour lamps analogous to mercury-vapour lamps; and J. Stark and R. Küch said that the glow is easily started when the zinc lamp is warmed to a rather higher temp. than is needed for cadmium. C. J. Hansen found the **boiling point** of zinc is 920° at 760 mm. press., and 550° in vacuo. F. Krafft also found the vap. press. of zinc is one atm. at 920°—K. Friedrich and A. Leroux gave 902°; W. R. Mott, 930°; J. Violle, 929·6° at 760 mm.; O. Ruff and B. Bergdahl, 930°; J. A. M. van Liempt, 931°; E. Becquerel, 930°; C. Barus, 905° to 929°; H. von Wartenberg, 918°; W. McA. Johnson gave 918° to 922°, or 919° at 743 mm. press.; and A. C. Egerton, 918°; if p mm. denotes a barometric press. near to 760 mm., D. Berthelot found the b.p. of zinc to be $918°+\frac{1}{8}(p-760)°$. F. Krafft and P. Lehmann gave for the b.p. of zinc the following temp. referred to mm. of mercury; and H. C. Greenwood the temp. referred to atm.:

	Pressure in mm.					Press. in atm.			
Press.	60	85	100	120	135	6·3	11·7	21·5	53
B.p.	545°	552°	553°	554°	650°	1120°	1230°	1280	1510°

C. Barus estimates the b.p. of zinc rises about 1·5° for every 10 mm. increase of press. above 760 mm. H. St. C. Deville said that zinc boils at 929° to 954° in dry air; at 916° to 925° in hydrogen; and at 1067° to 1079° in carbon dioxide. C. Féry distilled all the zinc from brass by heating an alloy containing 37 per cent. of zinc in an electric arc-furnace for two minutes. A. R. Haslam also made experiments on the fractional distillation of zinc from copper; and T. Turner and co-workers, on the effect of inert gases at different press. on the speed of volatilization. According to F. Braun, if brass be disintegrated at its m.p., the zinc distils from the particles. W. Sutherland calculated values of $dp/d\theta$ from C. Barus' vap. press. measurements and showed that the latent **heat of vaporization** of liquid zinc is 28·3 Cals. per gram-atom; W. McA. Johnson obtained 451 cals. per gram, and J. W. Richards, 426 cals.—approximately 33·7 Cals. per gram-atom. J. Traube, A. Wehnelt and C. Musceleanu, A. C. Egerton, and E. van Aubel also calculated values for this constant—the latter gave 365·8 cals. per gram; and J. A. M. van Liempt gave 31,430 cals. at the b.p. For the heat of sublimation, C. C. Person gave 1840 cals. E. Beckmann and O. Liesche measured the raising of the b.p. of zinc amalgams and found the results agreed with the monatomic condition of zinc at these temp. K. Bennewitz studied the **rate of evaporation** of molten zinc. W. G. Duffield gave $3·9\times10^4$ cms. per sec. for the velocity of the mols. projected from boiling zinc.

M. Knudsen found that the condensation of the vapour on a clean glass or mica surface has a critical temp. between −140° and −130° below which all the vapour is retained and above which an appreciable fraction is repelled. R. W. Wood and A. C. Egerton have also discussed the condensation of vapours on glass surfaces. As previously indicated, by cooling zinc vapour it can be condensed to a liquid; the more the vapour is diluted with air, the more difficult is this vapour to condense. When the temp. of the vapour falls below the m.p. of zinc, it solidifies in the form of a powder—*zinc fume* or *blue powder*. L. V. T. Lynen has stated that zinc vapour produced in the ordinary distillation process condenses between 415° and 550°; and W. Hempel, that the zinc vapour produced in the reduction of zinc oxide in the blast furnace, condenses below 470°. According to J. W. Richards, the dew-point of the vapour is the temp. at which it begins to deposit zinc, so that if the gas from the retort contains 57 per cent. of carbon monoxide and 43 per cent. of zinc vapour, the latter supports $760\times0·43$ or 327 mm. press., and from the table of vap. press.

of zinc, the mixture becomes sat. with zinc vapour at 847°, *i.e.* 83° below the normal b.p. of the metal. Similarly, a gas containing 12·8 per cent. of zinc vapour, 38·4 per cent. of carbon monoxide, and 48·8 per cent. of nitrogen, has the zinc vapour under a partial press. of 760×0·128 or 97 mm. The dew-point for that press., from the table of vap. press., is 745° or 185° below the normal b.p. of the metal. F. Krafft found drops of zinc exhibited Leidenfrost's phenomenon.

P. Drude [13] found zinc to be the most opaque of metals for sodium light. F. de la Provostaye and P. Desains found that zinc reflects 68 per cent. of normally incident lamp light, and P. Drude, 77 per cent. of red light. W. Meier estimated the following values for the **refractive index,** μ; the **index of absorption,** k, such that the amplitude of a wave after travelling one wave-length, λ, measured in the metal, is reduced in the ratio $1 : e^{-2\pi k}$, or, for a distance, S, in the ratio $1 : e^{-2\pi Sk/\lambda}$; and the percentage **reflecting power,** R, of zinc, when λ is less than unity; the values of R, when λ is greater than unity, are by W. W. Coblentz:

λ . . .	0·257	0·441	0·589	0·668	1·0	2·0	4·0	7·0	12·0
μ . . .	0·55	0·93	1·93	2·62	—	—	—	—	—
k . . .	0·61	3·19	4·66	5·08	—	—	—	—	—
R . . .	20	73	74	73	80	92	97	98	99

J. C. Jamin, L. Natanson, A. Beer, G. Quincke, S. Haughton, W. W. Coblentz, and W. Voigt have also made observations on the refractive index or on the reflecting power of zinc. For plane polarized light reflected from a polished surface with the **principal incidence,** ϕ, 80° 35′, the change is 90°, and if the plane polarized incident beam has a certain azimuth, **angle of principal azimuth,** ψ, 34° 35′, circular polarized light results. J. H. Gladstone's value for the **refraction equivalent** of zinc is 9·8; W. J. Pope's, 12·40 for the D-ray. J. Kanonnikoff, and A. Ghira have investigated this subject. C. Cuthbertson and E. P. Metcalfe found the refractivity of zinc vapour, $(\mu-1)\times10^6$, is 2070 for λ=518·3$\mu\mu$; 2150 for λ=546·0$\mu\mu$; 2060 for λ=589·3$\mu\mu$; and 1960 for λ=656·3$\mu\mu$. M. Faraday found that a film of zinc depolarized a ray of **polarized light** giving a red image which was reduced to a minimum by the rotation of the analyzer, and then converted to a blue image. S. Procopiu found that the birefringence is positive, but with finely divided cadmium suspended in toluene it is negative; and similarly with benzene, etc.

J. A. Wilkinson [14] observed no fluorescence during the action of chlorine, bromine, or iodine on zinc, but there is a bright green fluorescence when oxygen or sodium peroxide acts on the metal. The fluorescence is bluish-white with ammonium persulphate; greenish-white with zinc and sulphuric acid in electrolysis; and with zinc sulphate in the cathode rays there is a bluish-white fluorescence—E. Wiedemann and G. C. Schmidt say the latter is white. J. A. Crowther found the ratio of the coefficient of absorption of zinc, μ, for the **β-rays** to the density of the metal, is μ/D=6·95. H. R. von Traubenberg found the range of the **α-rays** in zinc to be $22·8\times10^{-4}$ cms. G. A. Sutherland and L. H. Clark measured the range of the β-rays in zinc. W. J. Russell and F. Soddy gave for the coeff. of absorption, μ, for the **γ-rays** of radium 0·228, or μ/D=3·93; for the uranium γ-rays, μ=0·329; for thorium-D γ-rays, μ=1·233; for mesothorium γ-rays, μ=0·53. The absorption of rays emitted by radioactive substances has also been investigated by K. W. F. Kohlrausch, A. Wood, V. J. Laine, J. Meyer, W. Schmidt, E. Riecke, H. A. Bumstead, etc. The emission of radiations by zinc and its alloys when heated in air to 100° and cooled have been studied by R. Blondlot. The secondary radiations emitted by zinc under the influence of **X-rays** have been studied by C. G. Barkla and co-workers, P. D. Innes, J. Borgmann, N. R. Campbell, J. C. McLennan, E. Hjalmar, R. Whiddington, K. Siegl, C. Füchtbauer, D. Hurmuzescu, etc. J. A. Becker studied the action of a magnetic field on the absorption of X-rays by zinc. The high frequency X-ray spectrum has been studied by H. G. J. Moseley, D. Coster, V. Dolejsek, E. Friman, etc. R. Blondlot found a phosphorescent screen of calcium sulphide glows more brightly when a piece of silver, copper, zinc, lead, or moist cardboard is placed near to it, but gold, platinum, glass, and dry cardboard are

inactive. E. A. Bichat found copper, zinc, and glass absorb **n-rays,** while platinum, silver, or aluminium do not. J. Stark and G. von Wendt studied the series spectra obtained by the action of the **canal rays.**

According to W. J. Russell,[15] polished zinc exerts a strong **photographic effect** on a photographic plate. B. Lengyel found the action more intense in moist carbon dioxide; it is feeble in air containing moist carbon dioxide, and in dry air free from carbon dioxide no action was observed in 16 hrs. G. W. A. Kahlbaum found the action to be dependent on the temp. as well as on the moisture; the radiations are said to pass through glass, and to be influenced by gravitation. B. L. Vanzetti found zinc to be less active than cadmium, but more active than aluminium, lead, or iron. R. Colson attributed the action to a slight vaporization of zinc at ordinary temp. H. Muraoka and M. Kasuya's experiments also agree with the assumption that the reducing action on the photographic plate is produced by vapour. F. Streintz and co-workers, A. Bryojawlensky, N. Piltschikoff, J. Blaas and P. Czermak, E. Rumpf, etc., have studied the action of zinc on potassium iodide, and on photographic plates. A. Nodon found that a sheet of zinc is opaque to the penetrating solar photogenic radiations, but a sheet of metal with a high valency is transparent.

W. Ramsay and J. F. Spencer[16] arrange the metals in the order Al, Mg, Zn, Sn, Cd, Pb, Bi, Au, . . . with respect to their **photoelectric effect** in air; K. Herrmann gives the order Al, Zn, Mg, Sn, Bi, Cd, Pb, Cu, . . . E. Ladenburg gave the order Cu, brass, Zn, Bi, . . . when tested in vacuo, and R. A. Millikan and G. Winchester gave Cu, Au, Ni, brass, Ag, Fe, Al, Mg, Sb, Zn, Pb. . . . The latter gave 0·197 volt at 26° for the positive potential assumed by the metal in vacuo under the influence of ultra-violet light. W. Hallwachs studied the effect of adsorbed gases. W. Frese found the photo-sensitiveness of zinc is greatly reduced by treatment with water or alcohol. R. Hamer found the limiting frequency for the photoelectric effect to be $\lambda=3426\pm74$.

The **spark spectrum** of zinc was examined by C. Wheatstone[17] in 1835, and H. F. Talbot, in 1836, noted some characteristic lines; A. Masson gave a drawing of the spectrum; and D. Alter, and A. J. Angström made further observations. G. Kirchhoff measured some of the spectral lines of zinc, and compared them with the Frauenhofer lines of the solar spectrum. T. R. Robinson made some inaccurate measurements of the spectral lines of zinc, but numerous accurate measurements have since been made by W. Huggins, R. Thalén, L. de Boisbaudran, E. Mascart, A. Cornu, J. N. Lockyer, G. D. Liveing and J. Dewar, W. N. Hartley and W. E. Adeney, J. S. Ames, H. Kayser and C. Runge, W. F. Meggers and K. Burns, G. A. Hemsalech and A. de Gramont, etc. The more important of the 73 lines in the arc spectrum of zinc, expressed in 10^{-8} cms. units, in air at 15° and 760 mm., are 3036, 3072, and 3345 in the ultra-violet; **4630·06, 4680·138, 4722·164, 4810·535,** and 4912 in the blue; **4925** in the greenish-blue; 6103 and **6362·345** in the orange. The lines numbered in clarendon type are illustrated in Fig. 10. F. Brasack claimed

Fig. 10.—The Spark Spectrum of Zinc.

to be able to detect 0·00000015 mgrm. of zinc by the spark spectrum. W. Schuler found that characteristic lines can be observed in the spark spectrum with 0·00002 mgrm. of zinc chloride; 0·00001 mgrm. of zinc bromide, iodide, nitrate, or sulphate. R. C. Dearle, and F. M. Walters studied the infra-red spectrum of zinc.

The spectra of magnesium, cadmium, and zinc embody a number of **line-series,** as illustrated in Fig. 3, Cap. Magnesium. H. Kayser and C. Runge represent the first two series of triplets in the spectrum of zinc by the formulæ:

FIRST SERIES.	SECOND SERIES.
$10^8\lambda^{-1}=42945{\cdot}32-131641n^{-2}-1236125n^{-1}$	$10^8\lambda^{-1}=42954{\cdot}59-126919n^{-2}-632850n^{-1}$
$10^8\lambda^{-1}=43331{\cdot}71-131641n^{-2}-1236125n^{-1}$	$10^8\lambda^{-1}=43343{\cdot}65-126919n^{-2}-632850n^{-1}$
$10^8\lambda^{-1}=43521{\cdot}48-131641n^{-2}-1236125n^{-1}$	$10^8\lambda^{-1}=43533{\cdot}32-126919n^{-2}-632850n^{-1}$

which account for 36 out of the 73 lines in the arc spectrum of zinc. The strong line 2138·3 which, according to J. Stark and S. Kinoshita, is the most intense line in the spectrum of zinc at a low temp., is not included in the formulæ; and several other intense lines are also not accounted for. The line-series in the spectrum of zinc have been studied by J. R. Rydberg, W. M. Watts, M. Reinganum, F. Paschen and E. Back, E. Hulthén, A. Kratzer, C. Runge and F. Paschen, A. S. King, L. Janicki, F. A. Saunders, N. A. Kent, P. G. Nutting, A. de Gramont, etc. E. Cappel studied the effect of *temperature* on the sensitiveness of the spectral reactions of zinc. The effect of *pressure* on the spectrum of zinc has been investigated by J. S. Ames and W. J. Humphreys; the *effect of hydrogen* by H. Crew, and R. A. Porter; and the last-named also studied the *effect of nitrogen;* and S. Procopiu various other gases. H. Finger, and B. de la Roche also studied the influence of the gaseous medium on the spectrum of zinc. A. Hagenbach and H. Schumacher studied the line spectrum of zinc in the electrodeless ring discharge tube. J. Formanek states that zinc salts do not give a *dauerndes und brauchbares* **flame spectrum.** G. D. Liveing and J. Dewar found no spectral lines when detonating gas is exploded in a zinc tube. W. N. Hartley found that the spectrum of zinc in the oxy-hydrogen flame is continuous. The flame spectrum of zinc has been investigated by A. Mitscherlich, A. Gouy, G. D. Liveing and J. Dewar, J. N. Lockyer, H. Ramage, P. Lewis, C. de Watteville, A. A. Michelson, M. Hamy, L. Janicki, etc. C. Ramsauer and F. Wolf studied the duration of the spectral lines in an extinguished arc. The **ultra-violet spectrum** of zinc has been investigated by G. G. Stokes, W. A. Miller, J. L. Soret, R. A. Sawyer, A. Cornu, G. D. Liveing and J. Dewar, L. Bell, G. Berndt, H. Deslandres, L. and E. Bloch, R. A. Millikan, F. Exner and E. Haschek, J. M. Eder and E. Valenta, E. Néculcéa, etc. According to A. de Gramont, the ultra-violet lines 3345·2, 3303·0, and 3384·4 are very sensitive and persist even with very small amounts of zinc. J. J. Dobbie and J. J. Fox found zinc vapour has some faint absorption bands in the ultra-violet. E. Hulthen studied the band spectrum of zinc. The **ultra-red spectrum** has been investigated by F. Paschen, H. Becquerel, etc. The **Zeeman effect** has been investigated by P. Zeeman, A. A. Michelson, T. Preston, H. M. Reese, K. Yamada, C. Runge and F. Paschen, A. Färber, A. Stettenheimer, P. Weiss and A. Cotton, W. A. Miller, H. Lunelund, A. Dufour, etc. F. L. Mohler and co-workers found the **resonance potential** of zinc vapour to be 4·18–5·65 volts, and the **ionization potential** 9·3 volts, and for the latter J. C. McLennan and J. F. T. Young gave 9·4 volts, K. T. Compton gave 3·07–3·74 volts for the minimum ionization potential. M. N. Saha has made observations on this subject. B. E. Moore studied the excitation stages in the arc spectrum of zinc.

According to J. Formanek,[18] soln. of zinc salts are colourless, and they give no **absorption spectrum;** but a neutral soln. of zinc chloride reacts with an alcoholic tincture of alkanna, and produces a reddish-violet soln. which has an absorption spectrum different from the tincture alone. W. N. Hartley found that a 200 cm. column of a soln. of a mol of zinc nitrate in a litre of water shows a complete absorption of rays with a wave-length beyond $\lambda=346$. P. Vaillant studied the absorption spectrum of zinc permanganate; and T. Retschinsky that of fused zinc chloride.

According to L. Weiller,[19] the **electrical conductivity** of zinc is 29·9 when that of silver is 100; G. Wiedemann gave 27·3; A. Matthiessen and A. von Bose, 29·02 at 0°; A. Emo, 26·991; and R. Benoit, 25·9 for the cold hammered metal. If the conductivity of mercury be unity, that of zinc at 0° is 15·88 to 15·99 according to A. Oberbeck and J. Bergmann; 17·52 at 0°, according to A. Matthiessen and A. von Bose; and 16·10, according to R. Benoit. The electrical conductivity in

reciprocal ohms when the value for mercury at 0° is $1{\cdot}063\times10^4$, was given by R. Haas as $17{\cdot}60\times10^4$ at 0°; by A. Sturm, as $18{\cdot}60\times10^4$ at 0°; by A. Oberbeck and J. Bergmann, as $16{\cdot}93\times10^4$; by W. Jäger and H. Diesselhorst, as $16{\cdot}51\times10^4$ at 18°, and $12{\cdot}59\times10^4$ at 100° for pure zinc, and $15{\cdot}83\times10^4$ at 18°, and $12{\cdot}13\times10^4$ for 98·6 per cent. zinc with 0·25 per cent. copper, and 1·1 per cent. lead. L. de la Rive gave for the conductivity of the solid at the m.p., $5{\cdot}43\times10^4$, and of the liquid at the m.p. $2{\cdot}7\times10^4$, and at 440°, $2{\cdot}69\times10^4$. A. Matthiessen and A. von Bose gave for the conductivity at θ°, $1-0{\cdot}0037047\theta+0{\cdot}0000082747\theta^2$; and C. Benedicks and R. Arpi, between 15° and 300°, $5{\cdot}45(1+0{\cdot}0039\theta+0{\cdot}0000017\theta^2)$ microhms. H. Tsutsumi found a marked decrease in the electrical conductivity of zinc during melting, as illustrated by Fig. 11, where the electrical conductivity is

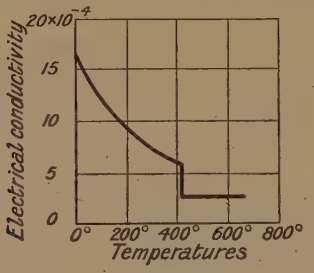

Fig. 11.—Electrical Conductivity. Curve of Liquid and Solid Zinc.

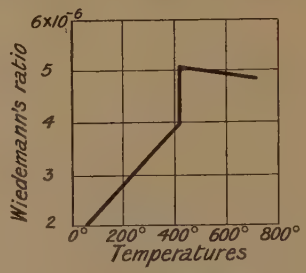

Fig. 12.—Wiedemann's Ratio of Liquid and Solid Zinc.

expressed in reciprocal ohms per c.c. Wiedmann's ratio, Thermal conductivity ÷ Electrical conductivity, is well satisfied for solid zinc, but fails completely with the metal in the liquid state.

The **electrical resistance,** R, in ohms per cm. cube, is the reciprocal of the conductivity. J. Dewar and J. A. Fleming found:

	0°	−50°	−77·8°	−100°	−150°	−191·1°	−200°	−252·9
R_θ . .	5·75	4·04	3·97	2·90	2·00	1·23	1·39	0·0511
R_θ/R_0 . .	1·00	0·703	0·691	0·504	0·348	0·314	0·242	0·0089

E. F. Northrup and V. A. Suydam found for temp. above atmospheric:

	100°	300°	415°	427°	450°	500° (l)	500° (s)	700°	850°
R . . .	7·95	13·25	17·00	37·30	37·08	36·60	35·90	35·60	35·74
R_θ/R_0 . .	1·38	2·30	2·96	6·49	6·46	6·36	6·25	6·19	6·21

H. le Chatelier found a transformation point in the electrical resistance of zinc between 340° and 350°; and C. Benedicks found two breaks in the temp.-resistance curve (*a*) between 160° and 170°, and (*b*) between 320° and 330°—the latter was identified with H. le Chatelier's point; this was confirmed by K. Monckmeyer and M. Werner. C. Benedicks and R. Arpi also confirmed the existence of the points *a* and *b*, and found a third point (*c*) at about 270°; they concluded that these points do not belong to pure zinc, but rather to zinc with cadmium as an impurity, and the points *a* and *b* mark the solubility limits of the homogeneous zinc-rich solid soln., while the third point *c* marks the eutectic arrest. This view is not confirmed by K. E. Bingham in her work on the electrical resistance of zinc which has been annealed at different temp. and then quenched. She found a critical point between 200° and 210°, and between 330° and 340°. The temp.-resistance curve of E. F. Northrup does not show these breaks. H. Tomlinson found the resistance of a zinc wire is increased if it is suspended with a load; and Lord Kelvin (W. Thomson), and J. Hopps observed the change in the resistance by twisting the wire; O. Chwolson found the resistance of a zinc wire decreased by annealing. The effect of *temperature* on the resistance of zinc has been measured by S. Kalischer,

F. Uppenborn, L. de la Rive, and by G. Vicentini with D. Omodei, and with C. Cattaneo. P. W. Bridgman gave 0·00416 for the temp. coeff., W. Jäger and H. Diesselhorst, 0·00412; and L. Holborn, 0·00415. The effect of *pressure* on the electrical resistance of zinc has been measured by E. Lisell, and by P. W. Bridgman. The latter found:

	0°	25°	50°	75°	100°
R	1·0000	1·1017	1·2050	1·3098	1·4159
Press. coeff. at 0 kgrm.	$-0{\cdot}0_5540$	$-0{\cdot}0_5533$	$-0{\cdot}0_5529$	$-0{\cdot}0_5526$	$-0{\cdot}0_5524$
Press. coeff. at 12,000 kgrms.	$-0{\cdot}0_5400$	$-0{\cdot}0_5394$	$-0{\cdot}0_5389$	$-0{\cdot}0_5387$	$-0{\cdot}0_5385$
Average	$-0{\cdot}0_54700$	$-0{\cdot}0_54634$	$-0{\cdot}0_54590$	$-0{\cdot}0_54562$	$-0{\cdot}0_54544$

E. Lisell gave for the press. coeff. at 0° $-0{\cdot}0_559$, against P. W. Bridgman's $-0{\cdot}0_5540$. O. Jaamaa and Y. E. G. Leinberg measured the resistance of powdered zinc mixed with marble.

The potential difference between zinc and other metals.—When a zinc rod is rubbed with a flannel, A. Macfarlane [20] found that it becomes feebly electronegative. The voltaic series of metals was arranged by A. Volta, T. Seebeck, J. C. E. Péclet, P. S. Munck af Rosenschöld, C. H. Pfaff, A. Gaugain, etc., and is in general agreement with . . . Al, Zn, Sn, Cd, Pb, Sb, Bi, nickel-brass, brass, Hg, Fe, . . . There are small differences in the position of some members of the series due possibly to the presence of impurities, nature of the surface, etc. The temp. has but little influence on the results. R. Kohlrausch measured the potential difference between zinc and other metals, that is, the **Volta effect** of zinc against different commercial metals, in volts at 18°:

	C	Cu	Fe	Pb	Pt	Sn	Zn amalgam	Brass
Zn	−1·096	−0·750	−0·600	−0·210	−0·281	−0·281	−0·144	−0·679
Zn amalgam	−1·208	−0·894	−0·744	−0·357	−0·125	−0·463	−0·144	−0·822

E. Gerland found for Zn : Cu, 100; Zn : Ag, 180·7; and Zn : Au, 115. Measurements have also been made by W. Hankel, R. B. Clifton, W. E. Ayrton and J. Perry, W. Hallwachs, J. L. Hoorweg, H. Pellet, F. Exner and J. Tuma, W. Thomson, E. Becquerel, J. Brown, and F. Schulze-Berge. The theory has been investigated by H. Greinacher, and E. Warburg and H. Greinacher. According to A. L. Hughes, zinc freed from occluded gases by distillation in vacuo is slightly electronegative to platinum, and it becomes electropositive as air is absorbed by the metal until a maximum value is attained.

A. Coehn and A. Lotz [21] found that zinc in vacuo is negatively charged against glass. T. Seebeck, W. Hankel, E. H. Hall, etc., have studied the e.m.f. developed by zinc coupled with other metals, and they placed it near copper and silver; A. Heil placed it between nickel and bismuth. E. Wagner found the **thermoelectric force,** or the **Seebeck effect,** of the *zinc-platinum couple* is 0·79 millivolt and the current flows from a junction at 100° to a junction at 0° to the platinum; J. Dewar and J. A. Fleming gave 0·77; W. Jäger and H. Diesselhorst, 0·75; K. Noll, 0·74; and W. H. Steele, 0·60. Lord Kelvin (W. Thomson) found the inversion with the Zn-Pt couple to be 8·2°. J. Dewar and J. A. Fleming gave for the *zinc-lead couple*, with one junction at 0° and the other at θ°, in C.G.S. units:

θ	100·2°	70·4°	50·4°	21·4°	7·5°	−3·3°	−80·6°	−204·8°
E.m.f.	+32390	+20920	+14100	+5140	+1620	−810	−17130	−33000

P. G. Tait gave for the Zn-Pb couple $2{\cdot}32+0{\cdot}0238\theta$ microvolts, or 2·79 microvolts at 20° and 3·51 at 50°. The neutral point is −98°. A. Matthiessen gave 3·7 microvolts for the thermoelectric power of the Pb-Zn couple; and K. Noll, 3·318 microvolts at 50°. P. W. Bridgman represented the Seebeck effect, E, with lead at atm. press. $E=(3{\cdot}047\theta-0{\cdot}00495\theta^2)\times10^{-6}$ volts. C. G. Knott studied the e.m.f. of the *zinc-iron couple*, and A. Palme found that the current attains a maximum of about one millivolt between 200° and 250°. Lord Kelvin found the current with a *zinc-gold couple* increases $0{\cdot}20\times10^{-6}$ volts per degree between 16° and 50°. No

breaks were found in the thermal e.m.f. and temp. curve of a zinc and iron couple by K. E. Bingham. E. Becquerel studied the *zinc-copper couple*. K. E. Bingham observed no breaks in the thermal e.m.f. of this couple, although P. N. Laschtchenko, S. F. Bykoff, and S. V. Efremoff obtained a critical value at 310° in the copper-zinc couple. A. Matthiessen studied the *zinc-silver couple*; K. Noll, *zinc-mercury couple*; and A. Heil, the *zinc-cupronickel couple*. P. W. Bridgman gave for the thermoelectric force, E volts$\times 10^6$, for a couple composed of uncompressed zinc, and zinc compressed to a press. p kgrms. per sq. cm., with the junctions at 0°:

		10°	20°	40°	60°	80°	100°
p	2,000	+1·1	+2·3	+4·8	+7·8	+10·8	+14·1
	6,000	3·6	7·3	15·3	24·0	33·3	43·0
	12,000	7·1	14·4	30·1	47·4	66·4	87·4

H. Jahn found for the **Peltier effect**—*vide* magnesium—with zinc against copper —0·68 millivolt, and E. P. le Roux, —0·45 millivolt. H. Jahn gave for the coeff. of the Peltier effect in calories per ampere-hour, —0·58 millivolt; E. P. le Roux, —0·39 millivolt; and E. Edlund, —0·01 millivolt. For the Peltier effect, P, of zinc against lead at atm. press., P. W. Bridgman gave $P=(3{\cdot}047-0{\cdot}0099\theta)(\theta+273)\times 10^{-6}$ volts; and for compressed and uncompressed zinc, the Peltier effect in joules per coulomb $\times 10^{-6}$, is:

		0°	20°	40°	60°	80°	100°
p	2,000	+30	+35	+41	+48	+50	+63
	6,000	98	110	131	150	169	190
	12,000	190	218	257	300	351	412

He also gave for the **Thomson effect**, σ, of zinc with lead at atm. press., $\sigma=0{\cdot}0099(\theta+273)\times 10^{-6}$ volts per degree; and for the excess in compressed over uncompressed zinc, in joules per coulomb per degree $\times 10^8$:

		0°	20°	40°	60°	80°	100°
p	2,000	+17	+18	+19	+20	+21	+22
	6,000	41	44	47	50	53	56
	12,000	63	89	118	148	183	220

E. Wagner made some observations on this subject up to 300 kgrms. per sq. cm. press. The **Hall effect** with zinc is $R=+0{\cdot}00082$. F. Unwin measured the effect of varying the strength of the magnetic field and of temp. on the Hall effect, and other thermo-magnetic phenomena. G. Borelius and F. Gunneson measured the Thomson effect in microvolts per degree, and found 5·9 at 380° K., 2·6 at 300° K., 1·25 at 200° K., 1·1 at 150° K., and 0·8 at 100° K. A. E. Caswell found for the coeff. of the Hall effect, $15{\cdot}33\times 10^{-13}$ at —24·7°; $8{\cdot}20\times 10^{-13}$ at 25·5°; $8{\cdot}38\times 10^{-13}$ at 32·6°; $8{\cdot}18\times 10^{-13}$ at 39·9°; $8{\cdot}23\times 10^{-13}$ at 41·2°; and $8{\cdot}23\times 10^{-13}$ at 76·7°. The coeff. of the **Ettingshausen effect** at 17·1° is 0; at 45·2°, $1{\cdot}76\times 10^{-8}$; at 60·7°, $2{\cdot}27\times 10^{-8}$; and at 76·7°, $3{\cdot}02\times 10^{-8}$. The coeff. of the **Nernst effect** at —16·2° is 290×10^{-12}; and at 37·2°, $-6{\cdot}25\times 10^{-12}$. The coeff. of the **Leduc effect** is $37{\cdot}59\times 10^{-7}$ at —16·2°, and 4×10^{-7} at 37·2°.

The potential difference between zinc and electrolytes.—According to R. B. Clifton,[22] a clear zinc plate is as strongly electropositive as copper towards water; if the metal is oxidized, it is negative towards water. N. R. Dhar gave 0·41 volt. W. Hankel also noted that the potential difference between zinc and *water* decreases as the metal is oxidized, and then increases. The action was also studied by W. F. Hillebrand and T. H. Norton. G. T. Fechner gave the series: Zn, Pb, Sn, Fe, Sb, Bi, Cu, Ag, Au. W. Ostwald found zinc to be electronegative towards the *haloid acids*, and *nitric, sulphuric, phosphoric, formic, acetic, propionic, oxalic, and benzoyl sulphuric acids*. J. C. von Yelin studied the action with nitric, sulphuric hydrochloric, phosphoric, acetic, *and tartaric acids*; H. Davy, J. C. Poggendorff, M. Faraday, S. Marianini, and G. Wetzlar, sulphuric acids; H. C. Oersted, sulphuric and nitric acid; H. E. Patten and W. R. Mott, the potential difference with nitric, sulphuric, hydrochloric, and *hydriodic acids*; A. A. de la Rive, and

M. H. Jacobi, nitric acid; J. C. Poggendorff, *hydrosulphuric acid;* M. Berthelot, *boric acid;* H. Davy, J. C. Poggendorff, and J. C. von Yelin studied the potential difference with aq. soln. of *potassium, sodium, and ammonium hydroxides;* F. Kunschert, M. Berthelot, and H. E. Patten and W. R. Mott with potassium hydroxide. G. T. Fechner, S. Marianini, J. C. Poggendorff, and J. C. von Yelin studied the potential difference with aq. soln. of *sodium and ammonium chlorides;* H. E. Patten and W. R. Mott, with aq. soln. of *potassium fluoride, potassium chloride* and sodium chloride, and *potassium bromide, and iodide;* L. Kahlenberg with aq. pyridine, and aniline soln. of *lithium chloride;* A. de la Rive, *calcium chloride;* E. Bouty, B. Neumann, G. Carrara and L. d'Agostini, J. Moser, with aq. soln. of *zinc chloride;* R. Salvadori studied *ethyl and methyl alcohol* soln. of potassium chloride; and G. Cararra and L. d'Agostini, methyl alcohol soln. of zinc chloride. C. M. van Deventer and H. van Lummel also compared the potential difference of zinc with salts in aq. and in alcoholic soln. R. Suchy studied the potential difference of zinc towards molten zinc chloride. J. C. Poggendorff studied the potential difference with aq. soln. of sodium sulphate; H. E. Patten and W. R. Mott, with aq. soln. of *potassium, ferrous, magnesium, cupric, cadmium, and zinc sulphates;* the effect with the last-named salt was also studied by G. de Villemontée, B. Neumann, F. Streintz and O. Strohschneider, W. Ostwald, J. Miesler, N. T. M. Wilsmore, F. Kunschert, F. Paschen, H. Pellat, H. J. S. Sand, A. C. Becquerel, L. Bleekrode, E. Kittler, J. Moser, J. von Hepperger, J. W. Müller, A. Eccher, H. F. Weber, S. Pagliani, M. Chanoz, M. Berthelot, and E. Bouty. M. Berthelot worked with aq. soln. of cupric sulphate. J. C. Poggendorff, M. Chanoz, and M. Berthelot studied the potential difference of zinc with an aq. soln. of *potassium sulphide.* The effect of *potassium nitrate* was studied by H. E. Patten and W. R. Mott, and with *zinc nitrate* by A. C. Becquerel, and E. Bouty and B. Neumann. The former also worked with soln. of *potassium phosphate;* P. S. Munck af Rosenschöld, E. Bouty, and H. E. Patten and W. R. Mott, with *potassium carbonate;* B. Neumann, L. Bleekrode, and J. Moser, with *zinc acetate;* H. E. Patten and W. R. Mott, with *potassium tartrate, chromate, and manganate; sodium silicate, and tungstate; potassium cyanate and thiocyanate;* and with *potassium cyanide.* M. H. Jacobi, L. Bleekrode, F. Spitzer, S. P. Thompson, and S. B. Christy also studied the effect with the last-named salt. M. Berthelot studied the effect of numerous other combinations. In illustration of the variable nature of the electrochemical series in the presence of different soln., M. Faraday gave:

H_2SO_4	Zn,	Cd,	Sn,	Pb,	Fe,	Ni,	Bi,	Sb,	Cu,	Ag
HNO_3 (dil.)	Zn,	Cd,	Pb,	Sn,	Fe,	Ni,	Bi,	Sb,	Cu,	Ag
HNO_3 (conc.)	Cd,	Zn,	Pb,	Sn,	Fe,	Bi,	Cu,	Sb,	Ag,	Ni
HCl	Zn,	Cd,	Sn,	Pb,	Fe,	Cu,	Bi,	Ni,	Ag,	Sb
KOH	Zn,	Sn,	Cd,	Sb,	Pb,	Bi,	Fe,	Cu,	Ni,	Ag
KSH	Cd,	Zn,	Cu,	Sn,	Sb,	Ag,	Pb,	Bi,	Ni,	Fe

G. Magnanini found the difference in potential in hundredths of a volt between zinc in a normal soln. of sulphuric acid and zinc in the following soln. containing n mols per litre: n-NaOH, −32·1 centivolts; n-KOH, −42·5; $\frac{1}{2}n$-Na_2SO_4, 1·4; n-$Na_2S_2O_3$, −5·9; n-KNO_3, 11·8 (variable); n-$NaNO_3$, 11·5; $\frac{1}{2}n$-K_2CrO_4, 23·9 (variable); $\frac{1}{2}n$-$K_2Cr_2O_7$, 72·8; $\frac{1}{2}n$-K_2SO_4, 1·8; $\frac{1}{2}n$-$(NH_4)_2SO_4$, −0·5; $\frac{1}{4}n$-K_4FeCy_6, −6·1; 0·167n-K_3FeCy_6, 41·0; n-KCyS, −1·2; $\frac{1}{2}n$-$Sr(NO_3)_2$, 14·8; $\frac{1}{3}n$-$Ba(NO_3)_2$, 21·9; n-$KClO_3$, 10–15; 0·167n-$KBrO_3$; n-NH_4Cl, 2·9; n-KF, 2·8; n-KBr, 2·3; $\frac{1}{2}n$-Na_2SO_3, 18·4; a soln. of bromine in NaOH, 18·4; n-tartaric acid, 5·5; $\frac{1}{2}n$-tartaric acid, 4·1; $\frac{1}{2}n$-potassium sodium tartrate, −7·9 centivolts. The sign of the difference of potential is such that the current flows from the more positive to the less positive metal through the external circuit. T. W. Richards and T. Dunham, and A. Smits measured the potential of zinc in various salt soln.

The potential difference of zinc against other metals in solutions of electrolytes.—Zinc is electropositive to most of the metals, but its character changes more or less when in the presence of electrolytes. On account of the high electropositive character of zinc, and its comparative cheapness, it is extensively employed as one element in galvanic batteries. H. Davy,[23] and J. C. Poggendorff found that zinc becomes more electropositive on amalgamation; and G. Lippmann found that

amalgamated zinc is electropositive towards ordinary zinc in a soln. of zinc sulphate, but there is no difference of potential against purified zinc when the soln. is neutralized with, say, barium carbonate. E. Cohen, and F. Fischer have measured the potential difference of purified zinc against zinc amalgam (90 per cent. mercury), and found 0·000488 volt at 0°, and 0·000750 volt at 25°. The difference of potential of zinc in contact with other metals in *sulphuric acid* soln. has been studied by J. C. Poggendorff, M. Faraday, H. Davy, G. T. Fechner, C. Wheatstone, R. B. Clifton, C. Hockin and H. A. Taylor, E. Kittler, B. G. Damien, and W. Wolff. The metals tried were tin, copper, silver, cadmium, iron, gold, or platinum against zinc or amalgamated zinc. H. C. Oersted found zinc in fuming sulphuric acid is first positive against lead, then negative, and finally positive. S. Marianini also tried sea-water acidified with sulphuric acid; E. Bouty, W. Wolff, C. Hockin and H. A. Taylor, and B. G. Damien tried zinc against carbon, lead, iron, cadmium brass, tin, copper, silver, gold, and platinum in aq. soln. of *zinc sulphate*. G. Tammann and W. Wiederholt measured against cadmium in zinc sulphate soln. K. E. Bingham found critical points at about 180° and 310° in the electrolytic potential curve of zinc against other metals in a 10 per cent. soln. of zinc sulphate. The zinc was annealed at different temp. and then quenched. B. G. Damien measured the electrolytic potential of zinc against copper in aq. soln. of *potassium, sodium, magnesium, or aluminium sulphate*. M. Faraday, C. Wheatstone, and J. G. Poggendorff tried zinc against copper and platinum in dil. *hydrochloric acid*. N. R. Dhar, G. T. Fechner, J. C. Poggendorff, and B. C. Damien investigated iron, copper, silver, and platinum against zinc or amalgamated zinc in soln. of *sodium, potassium, ammonium, barium, strontium, or zinc chloride*. J. C. Poggendorff, and B. G. Damien studied zinc against copper, iron, silver, and platinum in aq. soln. of *potassium bromide;* and of zinc against bismuth, tin, iron, copper, silver, and platinum in aq. soln. of *potassium iodide*. A. P. Laurie studied the potential of zinc against platinum in aq. soln. of *zinc iodide*, containing iodine. H. Davy, M. Faraday, A. A. de la Rive, A. Avogadro and V. Michelotti, and J. C. Poggendorff measured the potential difference of amalgamated zinc against copper and platinum in dil. *nitric acid;* B. G. Damien, zinc against copper in soln. of *potassium, sodium, ammonium, barium, or strontium nitrate;* W. Wolff, likewise, in soln. of *zinc nitrate;* and H. C. Oersted, of zinc against tin in soln. of *silver nitrate*. H. Davy, M. Faraday, B. G. Damien, and J. C. Poggendorff measured the difference of potential of zinc against antimony, iron, silver, and platinum in soln. of *potassium hydroxide*. P. S. Munck af Rosenschöld, J. C. Poggendorff, and B. G. Damien investigated the difference of potential of zinc against copper, tin, iron, and platinum in aq. soln. of *potassium and sodium carbonates*. J. C. Poggendorff, W. Skey, S. P. Thompson, and F. Kunschert found the potential difference of zinc against bismuth, iron, copper, silver, and carbon in aq. soln. of *potassium cyanide;* J. C. Poggendorff also worked with a soln. of *potassium ferrocyanide*. A. Naccari and M. Bellati studied zinc or amalgamated zinc against carbon in aq. soln. of *chromic acid*. E. Branly studied the difference of potential between zinc and copper in *glycerol;* A. Righi, in *petroleum* J. L. Hoorweg, in *stearic acid, paraffin, spermaceti, rape seed oil, shellac, wax*, and *sulphur;* and C. M. van Deventer and H. van Lummel, in *ethyl alcohol* and *propyl alcohol*. J. J. van Laar showed that the normal current between magnesium and zinc in aq. soln. can be reversed in alcoholic soln.

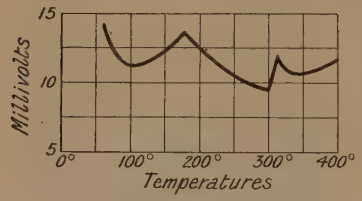

Fig. 13.—Electrolytic Potential Curve of Zinc Annealed at Different Temperatures.

M. H. Jacobi found zinc in nitric acid is electronegative against zinc, cadmium, tin, copper, or silver in a soln. of potassium cyanide; and electropositive against nickel, antimony, lead, mercury, bismuth, iron, platinum, or carbon in a soln. of potassium cyanide. J. C. Poggendorff studied the potential difference of zinc

or amalgamated zinc in dil. sulphuric acid against copper in a soln. of cupric sulphate, or platinum in nitric acid, or carbon in nitric or chromic acid. H. Buff studied the potential difference of zinc in a soln. of sulphuric acid against carbon, pyrolusite, pyrites, or cast iron in nitric acid ; he also studied zinc in a soln. of sodium chloride against platinum, copper, or zinc in a soln. of potassium polysulphide. J. P. Joule studied zinc in aq. potassium hydroxide against iron, coke, gold, or platinum in nitric acid, or copper in a soln. of cupric sulphate. J. Regnault studied zinc in a soln. of iodine in potassium iodide against carbon in a soln. of potassium iodide containing iodine, bromine, or chlorine; F. M. Raoult, $Zn : ZnSO_4$, $Pb(C_2H_3O_2)_2$; Pb. F. Streintz measured the potential difference of zinc in soln. of the nitrates against magnesium, aluminium, bismuth, cadmium, tin, lead, iron, nickel, cobalt, copper, and silver ; likewise also of zinc in soln. of the sulphates, or of the chlorides against these same metals. E. F. Herroun studied $Zn : ZnSO_4$, $SnSO_4 : Sn$; and also $Zn : H_2SO_4$, $SnSO_4 : Sn$; he also studied combinations with the two metals in soln. of the respective chlorides or iodides ; and of $Zn : ZnCl_2$, $Na_2PtCl_6 : Pt$, or of $Zn : ZnCl_2$, $AuCl_3 : Au$. Various other combinations have been studied by G. Magnanini, G. J. R. Blochmann, C. L. Speyers, C. R. A. Wright and C. Thompson, W. Beetz, and M. Berthelot. Latimer Clark's combination $Zn : ZnSO_4$, $Hg_2SO_4 : Hg$, with a sat. soln. of zinc sulphate has an e.m.f. at $\theta°$ of $1{\cdot}4328-0{\cdot}00119(\theta-15)-0{\cdot}000007(\theta-15)^2$ volt, and its use as a normal element has been discussed by W. Jäger, and H. Kahle. J. F. Daniell's cell $Zn : ZnSO_4$, $CuSO_4 : Cu$ has been discussed by J. C. Poggendorff, F. Fuchs, A. F. Svanberg, E. Branly, C. R. A. Wright, C. Fromme, E. Kittler, S. Carhart, C. Cattaneo, H. Pellat, F. M. Raoult, G. Meyer, W. H. Preece, F. Petruschefsky, etc.—*vide* **1.** 16, 3.

According to R. Suchy, Daniell's cell with molten salts instead of aq. soln. gives analogous results. Other combinations with molten salts have been investigated by O. H. Weber, R. Lorenz, etc.—*e.g.* V. Buscemi, W. Reinders, L. Poincaré, and J. Brown studied $Zn : ZnCl_2$, $SnCl_2 : Sn$; V. Czepinsky, $Zn : ZnBr_2$, $PbBr_2 : Pb$; R. Suchy, $Zn : ZnCl_2$; $AgCl : Ag$; V. Buscemi, $Zn : ZnCl_2$, $HgCl_2 : Hg$; W. Reinders, $Zn : ZnCl_2$, $PbCl_2 : Pb$; and J. Brown, $Zn : ZnCl_2$, $MgCl_2 : Mg$. E. Bouty found the temp. coeff. of the e.m.f. of zinc in fused zinc chloride.

T. W. Richards and G. S. Forbes, F. J. Mellenkamp, etc., have measured the potential of amalgamated zinc electrodes ; W. C. Moore measured the potential of the **zinc electrode** in the combination $Zn \mid ZnSO_4$ with the normal calomel electrode, at 20·1°—25·5°. For 0·5, 0·1, 0·01, and $0{\cdot}002N$-$ZnSO_4$ the observed electrode potentials are respectively —0·769, —0·790, —0·820, —0·838 volt. The values calculated from $E=0{\cdot}0292 \log (C_1/C_2)$ are respectively —0·780, —0·800, —0·829, and —0·850 volt. As W. A. Kistiakowsky has shown, it is necessary to exclude oxygen as completely as possible when setting up the zinc electrode. W. G. Horsch also measured the potential of the zinc electrode in the combination $Zn \mid ZnCl_2$; $AgCl \mid Ag$. E. Cohen and co-workers measured the effect of *pressure* and *temperature* on the e.m.f. of the zinc electrode ; H. Gilbault, and H. Wild, the effect of press.

The **heat of ionization** of zinc per valence is given by W. Ostwald [24] as 16,600 cals. The **transport numbers** of zinc ions have been measured by K. Drucker, F. Kohlrausch, W. Hittorf, G. Kümmel, S. Arrhenius, O. Grotrian, J. F. Daniell and W. A. Miller, J. C. d'Almeida, A. Chassy, etc. The **velocities of the ions,** V, expressed in mm. per sec., for a potential difference of one volt per mm., were determined by C. L. Weber for soln. containing n mols of zinc nitrate per litre :

n	0·2	0·1	0·04	0·02	0·01	0·005	0·0025	0·00125
V	0·091	0·111	0·095	0·077	0·084	0·051	0·052	0·051

W. P. Davey gave 0·76 A. for the **atomic radius** of the zinc ion in zinc oxide. J. E. Murray and B. Renault investigated the **electrochemical equivalent ;** the former found 0·0003287 grm. of zinc to be deposited per ampere-second.

The **decomposition voltages** of aq. soln. of many zinc salts—zinc sulphate,

bromide, phosphate, acetate, oxalate, tartrate, cyanide, and complex salts—have been determined by W. A. Kistiakowsky,[25] M. le Blanc, A. Gockel, W. Gaus, F. Kunschert, H. Jahn, J. E. Root, H. E. Patten and W. R. Mott, E. F. Smith and F. Mahr, etc. H. E. Patten measured the decomposition voltage of zinc chloride in acetone soln; R. Lorenz, and C. C. Garrard the decomposition voltage of molten zinc chloride and bromide. P. A. Favre, H. Jahn, and R. Colley investigated the relation between the thermal and electrical energy required for the decomposition of zinc salts. The electrolytic **solution pressure** of zinc in aq. salt soln. has been investigated by C. R. A. Wright and C. Thompson,[26] F. Braun, W. Ostwald, B. Neumann, M. le Blanc, R. A. Lehfeldt, F. Krüger, R. Abegg, C. M. van Deventer and H. van Lummel, etc.; and in alcoholic soln. by H. C. Jones and W. A. Smith, G. Carrara and L. d'Agostini, O. Sackur, etc. The constant works out approximately 10^{11} atm. for aq. soln., and $1{\cdot}9\times10^{10}$ in ethyl alcohol soln.

The **overvoltage** of hydrogen on zinc electrodes in N-H_2SO_4 is approximately 0·70 volt. The subject has been investigated by W. A. Caspari,[27] F. Kunschert, J. Tafel, E. Müller, A. Coehn and Y. Osaka, etc. The **polarization** of zinc electrodes has been investigated by R. Thöldte,[28] J. P. Joule, E. Patry, C. Matteucci, J. Regnauld, A. Oberbeck, K. R. Koch and A. Wüllner, W. J. Müller, T. W. Richards and T. Dunham, H. Buff, J. W. Langley, E. Edlund, F. Neumann, M. le Blanc, E. du Bois-Reymond, M. Corsepius, J. C. Poggendorff, etc. According to E. Beetz,[29] zinc does not become passive by the formation of a superficial film of oxide, because the oxide is electropositive towards copper and silver. W. J. Müller observed an abnormally high polarization in soln. containing OH'-ions, and this is regarded as evidence of **the passivity of zinc.** According to O. Sackur, and M. le Blanc and M. G. Levi, zinc becomes passive in complex soln. of cupric cyanide, or thiocyanate, in soln. of cadmium or nickel nitrate, or ferrous sulphate. W. R. Dunstan and J. R. Hill found that zinc is rendered passive towards soln. of copper sulphate, and towards aerial oxidation by immersion in a one per cent. soln. of potassium dichromate or chromate, or a 0·01–0·1 per cent. soln. of chromic acid. Two per cent. soln. of sodium carbonate or of borax also made zinc partly passive. The passivity is due to a surface film which can be removed by scratching. Washing with alcohol and drying also removes much of the passivity. A. Löb refers the alternating current passivity of zinc to the overvoltage of the hydrogen. A. Thiel attributed the inactivity of zinc to the formation of a black film of undissolved cadmium on the surface. M. Centnerszwer assumed that the period of induction observed when zinc dissolves in dil. acids is due to the passage of zinc from a passive to an active state. He found zinc becomes passive when heated in vacuo or in hydrogen. Since the metal thus treated is less active when rubbed with emery powder, than the untreated metal, he assumed that the passive condition extends below the surface. Active zinc becomes passive by anodic polarization in $2N$-sulphuric acid, and passive zinc becomes active by cathodic polarization—*vide* the potential of air-free zinc. U. Sborgi and P. Marchetti have studied the anodic behaviour of zinc in sat. soln. of lithium chloride in acetone. A. Günther-Schulze,[30] and W. Holtz have investigated the **electrolytic valve action** of zinc in aq. soln. of salts.

The **electric discharge** between zinc poles has been studied by C. E. Guye and A. Bron,[31] H. T. Barnes and A. N. Shaw, A. Pospieloff, F. Müller, and F. Ehrenhaft. M. Faraday, and E. Becquerel found zinc to be diamagnetic. The disintegration of zinc cathodes has been studied by B. Walter, and F. Braun. For the disintegration under liquids *vide* colloidal zinc. V. L. Chrisler studied the potential gradient of an arc with zinc electrodes; and A. Hörnli, the arc from zinc electrodes.

J. Königsberger found the **magnetic susceptibility** of zinc is $-0{\cdot}70\times10^{-6}$ to $-0{\cdot}94\times10^{-6}$ units of vol.; L. Lombardi found $-1{\cdot}0\times10^{-6}$ units of vol. C. Chéneveau found $-0{\cdot}10\times10^{-6}$ units of mass, and K. Honda found $-0{\cdot}15\times10^{-6}$ units of mass at 18°, and $-0{\cdot}10\times10^{-6}$ at 650°. T. Ishiwara found that the diamagnetic susceptibility of zinc shows a sudden decrease of about 4 per cent. at the m.p. and there is a linear decrease above and below this point.

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§ 5. The Physical Properties of Cadmium

Cadmium has a silver-white **colour** with a bluish-tinge, and a bright lustre, which soon dulls on exposure to air. According to A. Colson, a thin film of cadmium is bluish-violet in transmitted light. The vapour of cadmium is orange-yellow or yellowish-brown, and, according to F. Stromeyer, it produces no distinctive odour. H. Kämmerer [1] obtained silver-white **crystals** of cadmium, 6–8 mm. long, by distilling the metal in a stream of hydrogen in a combustion tube—the crystals occur as regular octahedrons, dodecahedrons, etc. F. Mylius and R. Funk obtained needle-like crystals and six-sided plates by sublimation of the metal in vacuo.

H. N. Morse and H. C. Jones, H. le Chatelier, E. de Souza, and G. W. A. Kahlbaum also obtained hexagonal crystals by sublimation and the crystals resembled those of zinc and magnesium. G. Rose and H. Kämmerer supposed the crystals to belong to the cubic system, but G. H. Williams, and P. Termier showed that the crystals are bipyramidal and belong to the hexagonal system; the axial ratio is given as $a : c = 1 : 1{\cdot}335$. G. d'Achiardi, and F. Rinne also made observations on the crystals. As indicated in connection with zinc, this metal and cadmium are isomorphous. According to W. Ortloff, the metals beryllium, magnesium, zinc, and cadmium, and also a large number of their compounds, form an eutropic series, and the increase in at. wt. is generally associated with an increase in sp. gr., mol. vol., index of refraction, and mol. refraction, but a decrease in hardness and sp. ht. The *c*-axis also changes with increasing mol. wt.:

	Be	Mg	Zn	Cd
At. wt. . . .	9·1	24·32	65·37	112·40
$a:c$	1 : 1·5802	1 : 1·6242	1 : 1·3564	1 : 1·3350

A. W. Hull found the **X-radiograms** of cadmium corresponded with a close-packed hexagonal lattice; they do not fit the hexagonal lattice with an axial ratio 1·335, but require an axial ratio 1·89. The side of the elementary triangular prism is 2·960 A., and the distance between the nearest atoms in the basal plane is 2·960 A., and in the pyramid plane, 3·280 A. The density obtained by dividing the mass of the atoms in an elementary cell, by the vol. of the cell, is 8·74, the observed value is 8·642. L. Hamburger made an ultra-microscopic examination of thin films of cadmium. S. Nishikawa and G. Asahara found that cadmium gives an abrupt change in the pattern of the X-radiogram at about 227°, and they studied the effect of rolling and annealing on the X-radiogram. W. L. Bragg calculated 1·60 A. for the atomic diameter and M. N. Saha 0·81 A. for the at. radius.

The cast metal is crystalline; and when sections are polished and etched with dil. nitric acid, or a soln. of cupric sulphate, or sulphuric acid with a few drops of nitric acid, the polygonal crystals are revealed. G. Cartaud found these crystals have the appearance of a mass of cells when a thin layer of cadmium is cast on a glass plate whereby the metal is suddenly cooled. According to H. Behrens, and W. Campbell, dendritic crystals appear on the surfaces of ingots when the crystals grow at the surface, and as the metal solidifies, the liquid part contracts, and sinks, leaving the dendrites standing in relief. The dendrites have the appearance of six-rayed stars, symmetrically arranged about a hexagonal axis, Fig. 14, and "from each axis, there grows a series of parallel branches making an angle of 60° with that axis, and therefore parallel to the next adjacent axis; between each pair of axes another axis begins thus adding to the hexagonal symmetry." M. Volmer, and M. Cook have studied the growth of crystals of cadmium; and G. Tammann and Q. A. Mansuri, the speed of crystallization of compressed powders at different temp., and in different atm.

Fig. 14.—Dendrites of Cadmium (×33).

G. T. Beilby showed that the surface of a crystalline metal which has been produced by breaking, tearing, or filing, by rolling, drawing, hammering, or polishing, is really covered with an amorphous glass-like film, which may be made to crystallize by mechanical treatment, or removed by suitable etching liquids. Zinc loses its crystalline structure when rolled or hammered into foil, or drawn into wire, but, according to S. Kalischer, the crystalline structure of cadmuim is not altogether lost by this treatment, and it is made more manifest by heating the metal between 200° and 250°, and etching as indicated above. By annealing the metal over 180°, W. Campbell obtained large polygonal crystals. J. A. Ewing and

W. Rosenhain annealed the metal at 200°. Z. Jeffries and R. S. Archer said that the lowest temp. at which the recrystallization of cold-worked cadmium has been observed is the room temp. J. N. Greenwood found the spontaneous annealing and recrystallization of chilled cast cadmium occurs at ordinary temp. The slower the cooling of the cast metal the larger the crystals. When cadmium is bent, it emits a crackling noise like tin. J. A. Ewing and W. Rosenhain found that after bending, the crystals show the slip-band structure previously described, and five such slip-bands can be seen in the bottom crystal, Fig. 15. According to F. Mylius and R. Funk, a cast plate of impure cadmium is not homogeneous, for the impurities may collect in separate aggregates. G. Tammann studied the etching of cadmium by a soln. of ammonium nitrate, and by hydrochloric acid.

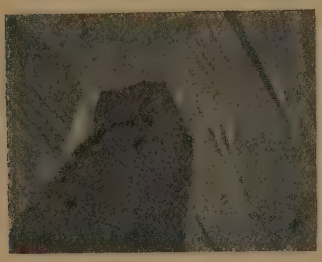

Fig. 15.—Cadmium Crystals showing Slip-bands.

The **specific gravity** of cadmium was given by J. G. Children [2] as 8·670; by J. F. John, 8·75; by W. Herapath as 8·650; by C. J. B. Karsten as 8·6355; by A. Baudrimont as 8·6689; by H. Kopp, 8·63; by H. Kämmerer, 8·52 to 8·69; and by H. G. F. Schröder between 8·540 and 8·667. A. Matthiessen gave 8·655 at 11°; G. Quincke, 8·627 at 0°; and G. Vicentini and D. Omodei, 8·6681 at 0°; W. Jäger and H. Diesselhorst, 8·63 at 18°. The best representative value is 8·642. According to F. Stromeyer, the cast metal has a sp. gr. 8·6040, and the hammered metal, 8·6944. J. G. Children, and H. G. F. Schröder also found the sp. gr. of the metal was increased by hammering, but F. C. A. H. Lantsberry found that the sp. gr. of annealed cadmium is 8·6437, and of the cold-worked metal, 8·6379; and J. Johnston and L. H. Adams gave 8·6397 for the sp. gr. of cadmium wire, and 8·6434 for the same after annealing. W. Spring found the sp. gr. of the metal at 17° is 8·642, and after it had been compressed at 20,000 atm., 8·667 at 16°, and no change occurred after a repetition of the treatment; G. W. A. Kahlbaum, K. Roth and P. Seidler also found the sp. gr. of distilled cadmium at 20°/4°, to be 8·6434, and after press., 8·64766; and when annealed at 270°, the sp. gr. was 8·6434, while a cold-drawn wire was found by G. W. A. Kahlbaum and E. Sturm to have a sp. gr. 8·6379. T. M. Lowry and R. G. Parker noted that the sp. gr. of the metal *en masse*, 8·6445, is greater than in the form of filings. This is in accord with the general behaviour of metals. The filings can be regarded as worked or hardened metal. When completely annealed, the metal contracts, but when partially annealed at say 100° or 108°, there is an expansion. T. A. Readwin noted the spontaneous change (expansion) of a coil of rolled cadmium; G. Quincke found the sp. gr. of the fused metal to be 8·394; H. Siedentopf, 7·9252; M. Töpler, 7·975; and T. R. Hogness gave $D=8·02-0·00110(\theta-320)$ for the sp. gr. of molten cadmium at $\theta°$. G. Vicentini and D. Omodei found the sp. gr. of the solid metal at 318° is 8·3665, and of the liquid metal at 318°, 7·987; there is therefore a contraction on solidification as was also observed by F. Nies and A. Winkelmann. R. Arpi gave

	349°	406°	466°	506°	550°	603°
Sp. gr. . .	7·94	7·88	7·82	7·78	7·74	7·69

from which the coeff. of expansion of the liquid can be computed. W. Broniewsky found the vol. changed 0·0472 part on melting. T. M. Lowry found the sp. gr. of cadmium is decreased by annealing at 100°. H. Ramage compared the sp. gr. of the metals beryllium, magnesium, zinc, cadmium, and mercury.

According to E. Cohen and W. D. Helderman,[3] when cadmium is heated for a considerable time in contact with a soln. of cadmium sulphate at 70° and 100°, its density decreases from 8·643 to 8·633 at 25°/4°, and the change is supposed to be due to an enantiotropic transformation which occurs at 64·9; and this is

supposed to account for the disintegration of cadmium wires heated to 80°, reported by A. Matthiessen and A. von Bose. The transition temp. varies according to the thermal history of the metal, and it is therefore inferred that more than two **allotropic forms** of cadmium are involved in the change. Electrolytically deposited Cd is unstable γ-cadmium, and this changes into stable α-cadmium in time. The change is attended by a decrease in the e.m.f. of a cell with the cadmium deposited on a Pt spiral as cathode, 12 per cent. cadmium amalgam as anode, and a soln. of cadmium sulphate as liquid. The e.m.f. at 25° fell from $E_\gamma=0{\cdot}05047-0{\cdot}0002437(\theta-25°)$ to $E_\alpha=0{\cdot}04742-0{\cdot}000200(\theta-25°)$ volts after standing several weeks. The difference thus increases as the temp. is lowered. The cadmium which gives the higher voltage is called γ-cadmium, and the one with the lower voltage α-cadmium. F. H. Getman also found that some cells give an e.m.f. of $E_\beta=0{\cdot}04862-0{\cdot}000201(\theta-25)$ volts a value slightly greater than α-cadmium, and it is concluded that cells with an e.m.f. of 0·050 volt contain γ-cadmium, those with an e.m.f. of 0·048, β-cadmium; and those with an e.m.f. of 0·047 volt, α-cadmium. The difference between the heat of dissolution of a gram-atom of γ- and α-cadmium in 8 per cent. amalgam at 18° is 729 cals., and this represents the heat evolved when γ-cadmium passes into α-cadmium. F. H. Getman gave 37·5° for the transition temp. of α- to β-cadmium. E. Cohen and A. Bruins, and F. H. Getman showed that the supposed allotropic changes cannot be attributed to the adsorption of water of soln. by the metal, but E. Cohen showed that F. H. Getman mistook a change in the cadmium amalgam from a homogeneous to a heterogeneous liquid, and if a recalculation be made the transition temp. α-Cd$\rightleftharpoons\beta$-Cd is nearly 60°. E. Cohen and W. D. Helderman showed that γ-Cd is in the metastable state between 0° and 100°. The e.m.f. of the cadmium cells correspond with the metastable transition point γ-Cd$\rightarrow\alpha$-Cd at 94·8°. For criticisms *vide* allotropic copper. J. N. Greenwood's observations on the annealing and hardness of cadmium led him to infer that there are two modifications of this element—α-Cd, stable between 20° and 65°; and β-Cd, stable above 65°. Observations were made up to 140°.

F. Stromeyer [4] found his metal to be harder than tin. A. Saposchnikoff and M. Sacharoff gave 15·9 kgrms. per sq. mm. for the **hardness** of cadmium. J. R. Rydberg gave for the relative hardness of magnesium, zinc, and cadmium, 2·0, 2·5, and 2·0. C. A. Edwards gave 29·0 for Brinell's hardness. P. Ludwik found the curve representing the variation of the hardness with temp. is regular and convex towards the temp. axis whether the metal be slowly or rapidly cooled. H. Siedentopf gave 80·835 to 83·18 mgrms. per mm., or 832·4 dynes per cm. for the **surface tension** of cadmium at 431°; and $a^2=20{\cdot}633$ to $20{\cdot}991$ per sq. mm. for the **specific cohesion**; G. Quincke gave 70·65 mgrms. per mm., or 815·2 dynes per cm. for the former, and $a^2=19{\cdot}8$ per sq. mm. for the latter—all in an atm. of carbon dioxide. W. Hagemann gave 553 dynes per cm. for the surface tension at 318°, 546·4 dynes per cm. at 350°, and 533·1 dynes per cm. at 412°. T. R. Hogness gave $\sigma=630-0{\cdot}065(\theta-320)$ for the surface tension of molten cadmium at θ°. For the coeff. of **viscosity** of molten cadmium at different temp., R. Arpi gave

	349°	406°	466°	506°	550°	603°
Viscosity	0·0144	0·0134	0·0127	0·0118	0·0115	0·0110

For the **diffusion constant** of cadmium in mercury, G. Meyer gave $k=1{\cdot}56$ at 15°; and M. von Wogau, $k=1{\cdot}45$ at 87°, and $k=2{\cdot}96$ at 99·1°. W. L. Bragg gave 0·160$\mu\mu$ for the at. radius of the at. spheres. K. F. Slotte estimated the edge of the mol. cube of liquid and solid cadmium to be $7{\cdot}1\times10^{-9}$ cms. C. T. Heycock and F. H. Neville estimated the **molecular weight** from the f.p. of soln. of cadmium in sodium, tin, lead, and bismuth. A. Masson found the **velocity of sound** in cadmium to be 2306·6 metres per sec.

F. Stromeyer [5] found the cadmium he prepared was easily cut with a knife; it was very flexible, and its **ductility** and **malleability** enabled it to be drawn into wires or beaten into plates. Like zinc at 205°, cadmium at 80° becomes brittle, and it can be powdered by rubbing it in a mortar. According to G. Wertheim,

Young's modulus, or the **modulus of elasticity** of cadmium, is from 424×10^6 to 531×10^6 grms. per sq. cm., or 4240 to 5310 kgrms. per sq. mm. at ordinary temp., and he found empirically that the product of Young's modulus into $(M/D)^{\frac{1}{3}}$ is approximately the same for all metals. P. Ludwik made some observations on this subject. W. Sutherland represented the relation between temp. $\theta°$ and Young's modulus, E, in grams per sq. cm., by $E/E_0=1-0{\cdot}823\theta/T$, where T is the m.p. on the absolute scale, and E_0 is the value of Young's modulus at absolute zero, *viz.* 1040×10^6 grms. per sq. cm. W. Voigt gave 7070, and E. Grüneisen 5090 to 5240 kgrms. per sq. mm. for the elastic modulus of cast cadmium; and E. Grüneisen, 4·99 dynes per sq. cm. According to the latter, also, the **volume elasticity,** *cubic elasticity*, or *bulk modulus*, is $4{\cdot}12\times10^{11}$ dynes per sq. cm. E. Grüneisen gave 0·30 for **Poisson's ratio**—that is, the transverse contraction to the longitudinal extension under tensile stress. B. MacNutt and A. Concilio discussed the noises which occur when cadmium is stressed above a certain load. The **compressibility** of cadmium is given by E. Grüneisen as 4200 kgrms. per sq. mm.; and T. W. Richards found the fractional change of vol. caused by one megabar press. between 100 and 500 megabars to be $2{\cdot}1\times10^{-6}$; E. Grüneisen gave $2{\cdot}4\times10^{-6}$ at 18°. S. Lussana found the coeff. of compressibility of cadmium was $2{\cdot}88\times10^{-6}$ at 11·5°, and $2{\cdot}99\times10^{-6}$ at 99°. L. H. Adams, E. D. Williamson, and J. Johnston gave $2{\cdot}24\times10^{-6}$ per megabar for the compressibility of cadmium at 0 megabar press., and $1{\cdot}70\times10^{-6}$ at 10,000 megabars press. They represented the change in vol., δv, per c.c. produced when the press. changes from p_0 to p by $\delta v=1{\cdot}2\times10^{-4}+2{\cdot}071\times10^{-6}(p-p_0)-1{\cdot}75\times10^{-11}(p-p_0)^2$. What N. S. Kurnakoff and S. F. Schemtschuschny call the **plasticity**—that is, the press. required to produce a flow of the metal through a given opening at ordinary temp.—is 31·00 kgrms. per sq. mm. W. Spring, and N. Werigen, S. Lewkojeff, and G. Tammann also measured the velocity of flow by pressing the warm metal through an opening. C. J. Burton and W. Marshall found that when suddenly compressed to 300 atm. the temp. of cadmium rises 0·285° and falls 0·293° when the press. is suddenly released.

According to A. Matthiessen,[6] the **coefficient of linear expansion** of cadmium between 0° and 100° is 0·00003159; and unit vol. at 0° becomes at $\theta°$ $1+0{\cdot}000080780\theta+0{\cdot}00000014000\theta^2$ vols. H. Fizeau gave 0·00003069 at 40°, or 0·00003102 between 0° and 100° for compressed powdered distilled cadmium; P. Glatzel found 0·00003121; C. Schäfer gave 0·00003060; and W. Voigt, 0·0000247 between 18° and 43°. F. C. Calvert and R. Johnson have also investigated the subject. H. Kopp gave 0·000094 for the coeff. of cubical expansion between 0° and 40°; and G. Vicentini and D. Omodei found 0·0000948 for solid cadmium at about 315°, and for the molten metal between 318° and 351°, 0·000170. N. E. Dorsey gave 0·00002970 at 10°, and 0·00002302 at −170°. W. Broniewsky gave 0·00009023 for the average coeff. of cubical expansion between absolute zero and the m.p. of cadmium. F. C. Calvert and R. Johnson found that if the **thermal conductivity,** λ, of silver is 100, that of cadmium is 57·7. F. Weber [7] gave 0·2213 for the absolute conductivity in cals. per cm. per sec. per degree difference of temp. and gave 0·2200 at 0°, and 0·2045 at 100°. W. Jäger and H. Diesselhorst gave 0·2216 at 18° for highly-purified cast cadmium, and 0·2149 at 100°; drawn wire gave a rather higher value. C. H. Lees obtained 0·217 at 18°; 0·219 at 0°; 0·228 at −80°; and 0·239 at −160°. L. Lorenz gave 0·0007046 for the temp. coeff. of the conductivity, and W. Jäger and H. Diesselhorst, −0·38 per cent. The latter also found the temp. conducting power—λ/Ds, where D is the sp. gr., and s the sp. ht.—to be 0·047 at 18° and 0·444 at 100°, with a temp. coeff. of −0·6 per cent. P. W. Bridgman found the thermal conductivity of cadmium increases linearly with press. R. Schott found the thermal conductivity, λ, and the electrical conductivity, K, of cadmium to increase as the temp. is reduced:

	0°	−186°	−250·7°	−251·9°	−252·6°
λ	0·975	1·033	1·833	1·852	1·872
K	0·00146	0·00536	—	—	0·00699

H. V. Regnault [8] found the **specific heat of cadmium** to be 0·0567; R. Bunsen, 0·0548 between 0° and 100°; W. Voigt, 0·0549 between 18° and 99°. H. Kopp gave 0·0542 at about 37°; A. A. de la Rive and J. Marcet, 0·058 at 10°; F. Weber, 0·0475; and C. J. Burton and W. Marshall, 0·055. E. Heilborn, and L. Sohncke deduced that the sp. ht. of an element with monatomic mol. must decrease with rise of temp., and this agrees with observations on the sp. ht. of mercury. L. Schüz found the sp. ht. of cadmium to be greater between −78° and 20° than between 20° and 100°, but A. Naccari found that the sp. ht. of cadmium steadily rises from 18° to 320°, and he gave 0·0546 at 0°; 0·0570 at 100°; 0·0588 at 200°; and 0·0607 at 300°, or, at θ°, the sp. ht. is $0{\cdot}0546+0{\cdot}000023670\theta$. U. Behn gave 0·0498 between −186° and −79°; 0·0537 between −79° and 18°; and between 18° and 100°, 0·056; G. W. A. Kahlbaum, K. Roth, and P. Siedler, 0·0559 for ordinary redistilled cadmium, and 0·0560 for cadmium which has been subjected to a high press. F. Streintz gave 5·6 for the at. ht. between −186° and −79°; and 6·0 between 79° and 18°; the temp. coeff. between −30° and −130° is 0·00071. E. H. and E. Griffiths found the at. ht., C_p, to decrease as the temp. falls, thus:

	−223°	−173°	−133°	−93°	−53°	13°	7°	47°	107°
C_p	3·46	5·37	5·79	5·93	6·04	6·14	6·19	6·29	6·44

W. H. Rodebush gave for the at. ht., C_p, 4·69 at −200°; 4·94 at −193°; 5·15 at −183°; 5·32 at −173°. A. Naccari represented his results for the sp. ht. of cadmium at θ°, by $0{\cdot}0546(1+0{\cdot}000443100\theta)$. R. C. Tolman gave 39·8 for the **entropy** of cadmium at 25°, G. N. Lewis and co-workers, 39·79 (gas), or solid 11·80.

The **melting point** of cadmium was found by A. D. van Riemsdijk,[9] and by F. Rudberg to be 320°; by A. Ditte, 315°; by B. Wood, 315°–316°; by C. C. Person, and H. L. Callendar, 320·7°; by F. Nies and A. Winkelmann, 310°–320°; by H. Becquerel, 315·8°; by G. Vicentini and D. Omodei, 318°; by E. H. Griffiths, 321·67°; by H. Siedentopf, 312°; by A. L. Day and E. T. Allen, 320·7° to 321·7°; by C. Schäfer, 320°; by L. Holborn and A. L. Day, 321·7°; by N. S. Kurnakoff and N. N. Pushin, 321·0°; C. W. Waidner and G. K. Burgess, 320·39° to 321·01°; A. L. Day and R. B. Sosman, $320{\cdot}0°\pm0{\cdot}3°$; and by L. Holborn and F. Henning, 320·92°. Other determinations have been made in connection with the fusion curves of binary mixtures by C. T. Heycock and F. H. Neville, H. Gautier, O. Boudouard, G. Masing and G. Tammann, H. C. Bijl, K. Lewkonja, R. Sahmen, M. Kobayashi, A. Stoffel, G. Hindrichs, D. P. Smith, C. H. Mathewson G. Voss, W. Treitschke, etc. According to K. Scheel, W. Guertler and M. Pirani, and L. I. Dana and P. D. Foote, the best representative value may be taken to be 321°. H. Ramage compared the m.p. of the metals beryllium, magnesium, zinc, cadmium, and mercury. M. Lémeray, J. von Panayeff, and H. F. Wiebe have also discussed the relations of the m.p. of these elements. W. Spring claimed to have united two cylinders of cadmium by warming them for 5 hrs. at 295°. J. Johnston and L. H. Adams found the m.p. of cadmium was depressed $d\theta/dp=0{\cdot}00629°$ per atm. G. G. Person gave 13·66 Cals. per kgrm. or 1·54 Cals. per gram-atom for the **heat of fusion** of cadmium; J. Johnston and L. H. Adams gave 13·7 cals. per gram. A. C. Egerton, and J. W. Richards have made observations on this subject. F. S. Mortimer gave 23·4 Cals. for the latent **heat of vaporization.**

C. Barus, and O. Ruff and B. Bergdahl measured the **vapour pressure** of cadmium in mm. of mercury at different temp., and the former found:

	549°	565°	620°	667°	702°	724°	745°	760°	770°
Vap. press.	22	26	75	157	262	355	489	624	766

J. W. Richards also calculated the following values for the vap. press. in mm. of mercury:

	183°	300°	367°	473°	600°	700°	780°	934°	1652°
Vap. press.	0·0002	0·050	0·478	9·23	75·75	300	760	3230	123120

The vap. press. curve of cadmium is indicated in Fig. 9. A. C. Egerton represented the vap. press., p, of cadmium at the absolute temp., T, by $p=5{\cdot}27\times10^{13}T^{-\frac{1}{2}}e^{2{\cdot}77\times10^4/RT}$ dynes per sq. cm., or $\log p=10{\cdot}5979-0{\cdot}5\log T-6060T^{-1}$ mm. The slope of the vap. press. curve of cadmium at the m.p. is $3{\cdot}70\times10^{-3}$ mm. J. A. M. van Liempt represented the vap. press., p, of cadmium between 822° K. and 1055° K. by the formula $\log p=-5977/T+5{\cdot}65$ atm., where T denotes the absolute temp.; and he represented the sublimation curve of cadmium by the formula $\log p=-6313/T+6{\cdot}21$. F. A. Henglein made some observations on this subject. C. Barus' formula is $\log p=2063-7443T^{-1}-3{\cdot}868\log T$; and H. Braune's, $\log p=-5753T^{-1}-1{\cdot}28\log T+12{\cdot}282$. J. A. M. van Liempt gave 25·82 for **Trouton's constant**; and H. Braune, 7·50 for the **chemical constant.**

According to B. Wood,[10] cadmium volatilizes at a temp. somewhat over 315°, "giving off orange-yellow coloured suffocating fumes, which, when inhaled too freely, leave a disagreeable, sweetish, styptic sensation upon the lips, and an intolerable and persistent brassy taste in the mouth, with constriction in the throat, heaviness in the head, and nausea." W. Spring supposed cadmium volatilizes between 295° and 300° because it can alloy with copper at that temp. C. J. Hansen found that cadmium evaporates appreciably at 429°. F. Krafft found that cadmium evaporates appreciably at 322°, and boils in vacuo at 450° when exposed to green cathode rays. E. Demarçay, and A. Schuller observed the vaporization at 160°. According to F. Krafft and L. Bergfeld, the difference between the temp., 156°, at which vaporization begins in vacuo, and the b.p., 450°, in vacuo, is approximately equal to the difference between the b.p. of the metal in vacuo and at atm. press. 749°. T. Turner and co-workers studied the effect of inert gases at different press. on the rate of volatilization of cadmium. K. Bennewitz measured the **rate of evaporation** of cadmium in vacuo. H. J. S. Sand, J. Stark and S. Kinoshita, and J. Stark and R. Kuch made a **cadmium vapour lamp** analogous to the mercury vapour lamp. F. Krafft found drops of cadmium exhibited Leidenfrost's phenomenon. C. J. Hansen found the **boiling point** of cadmium to be 749° at atm. press., and 450° in vacuo. H. St. C. Deville and L. Troost gave 860°, which on correction becomes 815°, for the b.p. of cadmium. T. Carnelley and W. C. Williams gave 763° to 772°; E. Becquerel, 746°; C. Barus, 782°; W. R. Mott, 778°; H. le Chatelier, 770°; O. Ruff and B. Bergdahl, 785°; J. A. M. van Liempt, 786°; D. Berthelot, 778°; O. H. Weber, 770° to 780°. C. Barus gave for the b.p. of cadmium at different press. in mm. of mercury:

Press.	0	22	105	262	489	517	656	756
B.p.	444°	549°	639°	702°	745°	750°	766°	772°

D. Berthelot represented the b.p. of cadmium by $788+\frac{1}{9}(p-760)$, where p denotes the press. but slightly removed from normal atm. press. in mm. of mercury. According to F. Krafft and P. Lehmann, the b.p. of cadmium increases 5° for a rise of 80° mm. press. W. Sutherland calculated values of $dp/d\theta$ from C. Barus' vap. press. measurements, and showed that the latent **heat of vaporization** of liquid cadmium is 29·6 Cals. per gram-atom. A. Wehnelt and C. Musceleanu, and E. van Aubel found the latent heat of vaporization of zinc is 181 Cals. per kgrm., J. W. Richards gave 216 Cals. per kgrm., and J. A. M. van Liempt, 27,360 cals. at the b.p. C. C. Person gave 1540 cals. for the heat of sublimation. E. Beckmann and O. Liesche measured the b.p. of cadmium amalgams and found the results agreed with the monatomic condition of the metal at these temp. W. G. Duffield gave $4{\cdot}0\times10^4$ cms. per sec. for the velocity of the mols. projected from boiling cadmium.

According to M. Knudsen, cadmium vapour condenses on a clean glass or mica plate when the temp. is between −183° and −78°, but above the latter temp., the vapour is partly retained by and partly repelled from the surface. R. W. Wood found that cadmium may condense as a thin metal film when the temp. is below −100°, but above that temp. it deposits aggregates of metal which appears to be clusters of crystals. A. C. Egerton has also made observations on this subject. According

to J. W. Richards, if the partial press. of cadmium vapour in a condenser is 380 mm., no metal will condense until the temp. of the gases is reduced to 720°. This temp. may thus be compared with the dew-point of air—*vide* zinc fume.

P. Drude [11] found the **index of refraction** of metallic cadmium to be $\mu=1{\cdot}13$ for $\lambda=0{\cdot}589\mu$; the **absorption index** $k=501$; and the **reflecting power** $R=85$ per cent. W. W. Coblentz gave for the reflecting power R:

λ . . .	1·0	2·0	4·0	7·0	10·0	12·0μ
R . . .	72	87	96	98	98	99

Plane polarized light reflected from a polished surface is generally elliptically polarized, and for a certain angle, the **angle of principal incidence,** ϕ, 79° 57′, the change is 90°, and if the plane polarized incident beam has a certain azimuth, **angle of principal azimuth,** ψ, 38° 53′, circular polarized light results. H. Knoblauch gave 76·65° for the polarization angle of heat rays, and 4·087 for the index of refraction; and for yellow rays respectively 70·00° and 2·747. C. Cuthbertson and E. P. Metcalfe gave for the refractivity $(\mu-1)\times10^6=2780$ for cadmium vapour with $\lambda=518{\cdot}3\mu\mu$; 2725 for $\lambda=546\mu\mu$; 2675 for $\lambda=589{\cdot}3\mu\mu$, and $\lambda=656{\cdot}3\mu\mu$. L. Natanson obtained 1337 for sodium light. C. V. Kent measured the effect of temp. on the optical properties of molten cadmium. J. H. Gladstone's value for the **refraction equivalent** is 13·1, and W. J. Pope's, 16·53 for the *D*-ray. J. Kanonnikoff, and W. Ortloff have made observations on this subject. B. Pogany measured the **Faraday effect,** that is, the **rotation of the plane of polarization** of thin films of cadmium. S. Procopiu found that toluene has a positive birefringence, but if finely powdered cadmium is suspended thereon, the birefringence is negative. Similarly with benzene, etc.

J. A. Wilkinson [12] observed a bright greenish-yellow **fluorescence** during the action of chlorine on cadmium but none with bromine or iodine; a yellow fluorescence during the action of oxygen or sodium peroxide; and a white or bluish-white fluorescence during the action of a persulphate. E. Wiedemann and G. C. Schmidt also examined the phosphorescence of cadmium salts in the cathode rays. J. S. van der Lingen studied the fluorescence of cadmium vapour. J. J. Thomson, H. G. J. Moseley, E. Hjalmar, and C. G. Barkla and C. A. Sadler have examined the absorption coeff. of cadmium under the influence of the secondary radiations from **X-rays;** and M. Hurmuzescu found that cadmium is less active than zinc, but more active than magnesium, aluminium, or tin. The high frequency or X-ray spectrum has been studied by E. Friman, D. Coster, etc. J. A. Becker investigated the effect of a magnetic field on the absorption of X-rays. N. R. Campbell has studied the ionization of air by the metal; and H. Greinacher, the radioactivity of cadmium. H. R. von Traubenberg found the range of the **α-rays** in cadmium to be $24{\cdot}2\times10^{-4}$ cms. F. Streintz, B. L. Vanzetti, H. Muraoka and M. Kasuya, F. Streintz and O. Strohschneider, and N. Piltschikoff have studied the **photographic effects** of cadmium on silver bromide, and potassium iodide. E. Légrady attributes the effect to a reaction with water vapour whereby H·-ions are produced, but no hydrogen peroxide is formed as assumed by W. Merckens—*vide* copper, and zinc. The elements arranged in the order of their **photoelectric effect** have been given in connection with zinc. R. Hamer found the limiting frequency for the photoelectric effect with cadmium to be 3130 ± 50.

Fig. 16.—The Spark Spectrum of Cadmium.

The **spark spectrum** of cadmium was first noted by C. Wheatstone.[13] Observations by A. Masson, and T. R. Robinson did not advance the study very far. G. Kirchhoff measured some lines and compared the results with the measurements

of the Frauenhofer lines of the solar spectrum. Measurements have been made by R. Thalén, W. Huggins, L. de Boisbaudran, J. N. Lockyer, W. N. Hartley, G. D. Liveing and J. Dewar, H. Becquerel, G. Ciamician, G. A. Hemsalech and A. de Gramont, E. Carter, J. S. Ames, H. Kayser and C. Runge, A. A. Michelson, A. Fowler and H. Payn, etc. The more important of the 74 lines in the arc spectrum of cadmium, expressed in 10^{-8} cm. units, in air at 15° and 760 mm., are: 3261. 3404, 3406, 3466, and 3611 in the ultra-violet; 3982 in the violet; 4413, 4678, and 4799·908 (β) in the blue; 5085·822 (α), 5155, 5338, and 5379 in the green; and 6438·470 (γ) in the red. The triplet on the scale at 80, 95·4, and 102·8 in the spectrum of cadmium corresponds with the triplet at 94·6, 100·05, and 102·6 in the spectrum of zinc. The α-, β-, and γ-lines are characteristic. With a more intense sparking, the α-line becomes weaker, and lines appear at 5379 and 5338. A. A. Michelson proposed referring measurements of wave-lengths of spectral lines to the α-, β-, and γ-cadmium lines. The red line at 6438 and the green line at 5086 serve as standards for absolute measurements. F. Brasack claimed to be able to detect 0·0004 mgrm. of cadmium in the spectrum of the spark from metal electrodes; and E. Cappel, 0·000056 mgrm. W. Schuler found the characteristic lines of cadmium are no longer visible with 0·0004 mgrm. of cadmium chloride; 0·0002 mgrm. of cadmium bromide, iodide, nitrate, or sulphate. R. C. Dearle, and F. M. Walters measured the infra-red spectrum of cadmium.

The spectral lines of the magnesium, zinc, and cadmium family of elements furnish a number of **line-series,** as illustrated in Fig. 3, **4.** 29, 4. H. Kayser and C. Runge represented the first two series of triplets in the spectrum of cadmium by the formulæ:

FIRST SERIES.	SECOND SERIES.
$10^8\lambda^{-1}=40755{\cdot}21-128635n^{-2}-1289619n^{-1}$	$10^8\lambda^{-1}=40797{\cdot}12-126146n^{-2}-555137n^{-1}$
$10^8\lambda^{-1}=41914{\cdot}60-128635n^{-2}-1289619n^{-1}$	$10^8\lambda^{-1}=41968{\cdot}80-126146n^{-2}-555137n^{-1}$
$10^8\lambda^{-1}=42456{\cdot}64-128635n^{-2}-1289619n^{-1}$	$10^8\lambda^{-1}=42510{\cdot}58-126146n^{-2}-555137n^{-1}$

which account for nearly half of the lines in the arc-spectrum of cadmium. Several intense lines are not included in the formulæ, *e.g.* the line 2288·10 which, according to J. Stack and S. Kinoshita, is the most intense of the cadmium lines at a low temp. The line-series of the cadmium spectrum have been studied by W. N. Hartley, J. S. Ames, J. R. Rydberg, H. Kayser and C. Runge, C. Runge and F. Paschen, L. Janicki, A. Grünwald, C. de Watteville, J. de Kowalsky and P. Joye, E. Hulthén and E. Bengtsson, S. Procopiu, A. Kratzer, H. Crew, A. Fowler and H. Payn, O. von Bäyer, F. A. Saunders, P. G. Nutting, etc. C. Fabry studied the satellites in the cadmium spectrum. J. M. Eder and E. Valenta, W. N. Hartley, C. de Watteville, E. Cappel, etc., studied the effect of *temperature* on the sensitiveness of the spectral reactions of zinc; the effect of *pressure* was investigated by A. Kalähne, M. Ritter, F. L. Mohler, W. J. Humphreys, C. Keller, etc.; the effect of *hydrogen* and *nitrogen* was studied by L. Arons; and H. Finger, and B. de la Roche, the effect of the gaseous medium on the spectrum. A. Hagenbach and H. Schumacher studied the line spectrum of cadmium in the electrodeless ring discharge.

The **flame spectrum** of cadmium consists of lines and bands which have a complicated structure. The lines include the 5086, 4800, 4678, and 3261. H. Ramage could not find the line 2288 in the oxy-hydrogen flame spectrum. The flame spectrum has been studied by A. Mitscherlich, J. N. Lockyer and W. C. Roberts, A. Gouy, J. M. Eder, W. N. Hartley, W. N. Hartley and H. Ramage, C. de Watteville, etc. The **ultra-violet spectrum** was investigated by G. G. Stokes, W. H. Miller, J. L. Soret, W. N. Hartley and W. E. Adeney, L. and E. Bloch, L. Bell, H. Deslandres, G. D. Liveing and J. Dewar, J. M. Eder, J. M. Eder and E. Valenta, G. Berndt, C. Runge and F. Paschen, R. A. Sawyer, E. Néculcéa, R. W. Wood and D. V. Guthrie, F. Exner and E. Haschek, J. Stark and S. Kinoshita, E. Mascart, etc. J. J. Dobbie and J. J. Fox found cadmium vapour has a number of sharply defined absorption bands in the ultra-violet. E. Hulthen studied the band spectrum of cadmium.

The **ultra-red spectrum** was investigated by V. Schumann, F. Paschen, H. Becquerel, etc. The **Zeeman effect** was investigated by A. A. Michelson, P. Zeeman, J. S. Ames, R. F. Earhart and H. M. Reese, T. Preston, J. C. Shedd, H. M. Reese, H. Ramage, W. H. Miller, C. Runge, F. Paschen and C. Runge, etc. Cadmium salts form colourless soln. which do not give an **absorption spectrum** alone or with tincture of alkanna. T. Retschinsky found solid cadmium chloride gives an absorption spectrum. J. Elster and H. Geitel have studied the **photoelectric effect** with cadmium. J. S. van der Lingen studied the electrodeless discharge in cadmium vapour. F. L. Mohler and co-workers found the **resonance potential** of cadmium vapour to be 3·95–5·35 volts, and the **ionization potential** to be 9·0 volts; for the latter, J. C. McLennan and J. F. T. Young obtained 9·0 volts. K. T. Compton found 2·66–3·96 volts for the minimum ionization potential. M. N. Saha has made observations on this subject. B. E. Moore studied the excitation stages in the arc spectrum of cadmium.

The **electrical conductivity** of cadmium has been measured by A. Matthiessen,[14] who found that if hard silver has a conductivity of 100, at 0°, that of cadmium is 22·10; E. Becquerel found 24·58; J. R. Benoit, 22·5; and A. Matthiessen and A. von Bose, 23·72; the latter also obtained $1-0{\cdot}0036871\theta+0{\cdot}0000075750\theta^2$ for the conductivity at $\theta°$; and J. R. Benoit, $1+0{\cdot}004264\theta+0{\cdot}0000017650\theta^2$. F. Weber found the specific conductivity to be 0·001461; W. Jäger and H. Diesselhorst gave for cadmium with less than 0·05 per cent. of lead, zinc, and iron, at 18°, $13{\cdot}13\times10^4$ rec. ohms, and at 100°, $9{\cdot}89\times10^4$ rec. ohms, while for the less pure metal, they obtained $13{\cdot}25\times10^4$ and $10{\cdot}18\times10^4$ rec. ohms respectively at 18° and at 100°; for the two varieties of cadmium the **electrical resistance** at $\theta°$ was found to be respectively $1+0{\cdot}00425\theta$, and $1+0{\cdot}0040\theta$. L. Lorenz obtained $14{\cdot}41\times10^4$ rec. ohms at 0°; G. Mayrhofer, $14{\cdot}7\times10^4$ rec. ohms at 0°; and the latter found that the conductivity increases 1·3 per cent. when the temp. was raised to 130°, and he gave for the specific conductivity at $\theta°$, $1-0{\cdot}00378\theta$. J. Dewar and J. A. Fleming found the electrical resistance R of cadmium in microhms to be:

$\theta°$ . .	182·2°	91·10°	18·8°	1·00°	−46·2°	−81·9°	−197·1°
R . .	18·367	13·843	10·980	10·064	0·286	6·945	2·952

A. Eucken and G. Gehlhoff gave 7·76 microhms at 0°; 5·45 at −79°; and 1·98 microhms at 190°. Some results by R. Schott are indicated in connection with thermal conductivity. E. F. Northrup and V. A. Suydam found, for the resistance R in microhms:

$\theta°$ . .	300°	325°	350°	400°	500°	600°	700°
R . .	16·52	33·76	33·60	33·70	34·12	34·82	35·78

and they gave the ratio 1·97 for the resistivity of the liquid at the m.p. (318°), *viz.* 33·77 microhms, to the value for the solid at the m.p. of zinc—*viz.* 17·1 microhms. G. Tammann and K. Dahl studied the relation between the resistance and structure of cadmium-zinc alloys. G. Vassura found the conductivity of cadmium at the m.p. 318°, before and after fusion, to be respectively $5{\cdot}69\times10^4$ and $2{\cdot}88\times10^4$ microhms, and G. Vicentini and D. Omodei gave for fused cadmium at the m.p. 318°, $2{\cdot}99\times10^4$ microhms.

F. Streintz found the temp. coeff. of the electrical resistance of cadmium between 18° and 100° to be $dR/d\theta=425\times10^{-5}$; L. Holborn gave 424×10^{-5} per degree between 0° and 100°. P. W. Bridgman, and B. Beckman measured the effect of *pressure* and temp. on the electrical resistance of cadmium; the former obtained for 0 and 1200 kgrms. per sq. cm.,

		0°	25°	50°	75°	100°
Resistance . . .		1·0000	1·1012	1·2057	1·3133	1·4240
Press. coeff.	0 kgrm.	$-0{\cdot}0_41063$	$-0{\cdot}0_41082$	$-0{\cdot}0_41095$	$-0{\cdot}0_41102$	$-0{\cdot}0_41106$
	12,000 kgrms.	$-0{\cdot}0_5746$	$-0{\cdot}0_5765$	$-0{\cdot}0_5778$	$-0{\cdot}0_5786$	$-0{\cdot}0_5790$
	Average .	$-0{\cdot}0_58940$	$-0{\cdot}0_59104$	$-0{\cdot}0_59212$	$-0{\cdot}0_59257$	$-0{\cdot}0_59270$

The average temp. coeff. from 0° to 100° at 0 kgrm. press. is 0·00424; W. Jäger

and H. Diesselhorst gave 0·00396 to 0·00421 ; and B. Beckman, 0·00425. G. Fäc found the influence of *magnetization* on the electrical resistance of cadmium to be uncertain. N. Dagostino found that the electrical resistance is increased by transverse magnetization, and L. Grunmach said that the increase is greater with cadmium than with zinc, copper, silver, gold, tin, lead, platinum, palladium, and tantalum.

A. Coehn and A. Lotz found that cadmium in vacuo is negatively charged against glass. W. Hankel[15] found that if the difference of potential of zinc and copper be 200, that of filed cadmium and copper is 175, and of cleaned cadmium, 181. The **Volta effect** was attributed by E. Warburg and H. Greinacher to a condensed layer of water because the difference of potential between cadmium and radiotelluro-copper is —0·540 volt, and when thoroughly dried, —0·015, and when exposed to the air of a room, —0·719. W. Ostwald found that cadmium, like zinc, is electronegative towards acids ; and W. Hankel that it is electronegative towards water. W. Spring found that cadmium which has been strongly compressed shows a difference of potential of 0·20 millivolt towards the annealed metal.

Cadmium is thermoelectrically positive. A. Seebeck[16] found that cadmium is nearer than zinc to the positive end of the thermoelectric series of metals, but, according to W. Hankel, it is less positive than iron or antimony, and, according to B. Bachmetjeff, it is more positive than indium. N. A. Hesehus found that when cadmium is warmed in a circuit of the metal, a current flows from the warm to the cold part, and the e.m.f. is smaller with cadmium than with antimony, and larger than with zinc, silver, copper, or brass. For the *cadmium-platinum couple* with the cold and hot junctions respectively at 0° and 100°, W. Jäger and H. Diesselhorst gave 0·85 millivolt ; J. Dewar and J. A. Fleming, 0·92 millivolt ; K. Noll, 0·88 millivolt ; W. H. Steele, 0·90 millivolt ; and E. Wagner, 0·92 millivolt. K. Noll found the **thermoelectric force,** or the **Seebeck effect,** of hard-drawn *cadmium-mercury couple* between 0° and 100° to be 875·09 millivolts, and with annealed cadmium, 859·74 millivolts. W. H. Steele, and J. Dewar and J. A. Fleming found the thermo-electric force of a *cadmium-lead couple* with one junction at 0° and the other at $\theta°$ is, in C.G.S. units :

θ . . .	100·2°	61·2°	8·1°	—4·0°	—34·6°	—85·2°	—128·8°	—205·0°
E.m.f. . .	48020	24600	2220	—1180	—8560	—17200	—21450	—26940

P. G. Tait found that with the cadmium-lead couple, the thermoelectric force at $\theta°$ is $2·63+0·0424\theta$, and the neutral point is —62°. P. W. Bridgman gave $E=(12·002\theta+0·1619\theta^2)\times10^{-6}$ volts for the Seebeck effect with cadmium and lead at atm. press. G. Borelius and F. Gunneson measured the Thomson effect between —176° and 94°. A. Heil measured the e.m.f. of a *cadmium-cupro-nickel couple* and found for $\theta°=230°$, +0·0117 volt. W. Jäger and H. Diesselhorst found for the *cadmium-copper couple*, +2·3 microvolts per degree between 0° and 100° ; for the *cadmium-iron couple*, +6·3 microvolts ; and for the *cadmium-constantin couple*, 49·4 microvolts. P. Cermak also studied the last-named thermocouple ; and A. Abt, the thermoelectric force between cadmium and copper, or carbon. For the Seebeck effect with a couple composed of one branch of uncompressed cadmium and the other of cadmium compressed to a press. p kgrms. per sq. cm., with the junctions at 0°, P. W. Bridgman found

		10°	20°	40°	60°	80°	100°
p	2,000 . . .	+0·14	+0·42	+1·38	+2·82	+4·74	+7·12
	6,000 . . .	0·88	2·10	5·48	8·88	15·14	21·16
	12,000 . . .	3·16	6·68	14·72	23·92	34·20	45·56

The effect is large and positive rising with temp. and press. The results are much affected by hysteresis, corresponding with an incomplete state of internal equilibrium. The **Peltier effect,** that is, the heat produced by a current at the junction of copper and cadmium, in cals. per ampère-hour—*vide* magnesium—is —0·62, according to H. Jahn, and —0·46, according to E. P. le Roux ; and the latter gave —0·45 millivolt for the Peltier e.m.f. ; H. Jahn gave —0·72 millivolt ; and E. Edlund, —0·16

millivolt. For the Peltier effect, σ, with cadmium and lead, P. W. Bridgman gave $\sigma=0{\cdot}3238(\theta+273)\times10^{-6}$ volts per degree, and for the Peltier effect between compressed and uncompressed cadmium, in joules per coulomb $\times10^6$:

		0°	20°	40°	60°	80°	100°
p	2,000	+3·8	+10·0	+18·8	+28·0	+38·1	+48·5
	6,000	18·6	41·0	61·6	80·7	99·8	118
	12,000	81·3	108	135	162	191	221

The effect is positive and rises with temp. and press. For the **Thomson effect,** excess in compressed over uncompressed cadmium, in joules per coulomb per degree $\times10^8$, P. W. Bridgman found:

		0°	20°	40°	60°	80°	100
p	2,000	+16	+35	+41	+37	+35	+45
	6,000	109	94	78	70	67	63
	12,000	105	99	94	90	90	93

The effect is positive and rises with temp. at low press., but falls at high press. E. Wagner also made some observations on this subject with press. up to 300 kgrms. per sq. cm. G. Borelius and F. Gunneson found the Thomson effect in microvolts per degree to be 9·8 at 400° K., 7·1 at 300° K., 0·55 at 190° K., 0·0 at 150° K., and —0·65 at 110° K. A. E. Caswell found for the coeff. of the Hall effect $8{\cdot}50\times10^{-13}$ at 42°; and $11{\cdot}67\times10^{-13}$ at 49·3°; for the coeff. of the Ettinghausen effect, $5{\cdot}96\times10^{-8}$ at 51·2°; for the coeff. of the Nernst effect, 0 at 39·4°; and for the coeff. of the Leduc effect, $1{\cdot}87\times10^{-7}$ at 39·4°.

W. G. Horsch[17] measured the potential of the amalgamated and ordinary **cadmium electrode** in the combinations $Cd_{amalgam}\,|\,CdCl_2,\,AgCl\,|\,Ag$, and $Cd\,|\,CdCl_2\,|\,Cd_{amalgam}$. E. Cohen and co-workers measured the effect of *pressure* and *temperature* on the electrode. The potential of cadmium against aq. soln. of various *cadmium salts* has been measured by B. Neumann, W. Nernst, U. Sborgi and A. Donati, W. Ostwald, G. Carrara and L. d'Agostini, F. Streintz and O. Strohschneider, N. R. Dhar, N. T. M. Wilsmore, F. M. G. Johnson and N. T. M. Wilsmore, F. Förster, C. Immerwahr, L. Kahlenberg, S. Labendzinsky, H. Euler, etc.—*vide* cadmium amalgam. The effect of temp. on the difference of potential between cadmium and aq. soln. of its salts was measured by E. Bouty and A. Gockel. F. M. G. Johnson and N. T. M. Wilsmore measured the potential of cadmium against soln. of cadmium nitrate in *liquid ammonia;* R. Luther, and G. Carrara and L. d'Agostini, with soln. of cadmium salts in *methyl and ethyl alcohols;* and L. Kahlenberg, with soln. of cadmium salts in aq. *pyridine.* R. Beutner, and F. Haber measured the difference of potential with cadmium and its compressed solid salts; and J. Brown, with fused cadmium chloride.

G. Magnanini measured the difference of potential, in centivolts, of zinc in a normal soln. of sulphuric acid against cadmium in a soln. containing n mols of the following salts per litre, and found $\frac{1}{2}n$-H_2SO_4, 36·6 centivolts; n-NaOH, 19·5; n-KOH, 15·5; $\frac{1}{2}n$-Na_2SO_4, 35·6; n-$Na_2S_2O_3$, 24·1; nKNO$_3$, 31·9; n-$NaNO_3$, 32·3; $\frac{1}{2}n$-K_2CrO_4, 42·8; $\frac{1}{2}n$-$K_2Cr_2O_7$, 61·1; $\frac{1}{2}n$-K_2SO_4, 34·7; $\frac{1}{2}n$-$(NH_4)_2SO_4$, 37·1; $\frac{1}{4}n$-K_4FeCy_6, 33·6; $0{\cdot}167n$-K_3FeCy_6, 80·8; n-KCyS, 32·5; $\frac{1}{2}n$-$Sr(NO_3)_2$, 38·3; $\frac{1}{3}n$-$Ba(NO_3)_2$, 39·3; $\frac{1}{5}n$-$KClO_3$, 39·9; $0{\cdot}167n$-$KBrO_3$, 40·7; n-NH_4Cl, 32·4; n-KF, 22·5; n-NaCl, 31·9; n-KBr, 31·7; n-KCl, 32·1; $\frac{1}{2}n$-Na_2SO_3, 28·7; soln. of bromine in sodium hydroxide, 41·6; n-tartaric acid, 39·7; $\frac{1}{2}n$-tartaric acid, 41·3; and $\frac{1}{2}n$-potassium sodium tartrate, 31·5.

Cadmium is strongly electropositive, and, according to J. C. Poggendorff,[18] it becomes less electropositive by amalgamation. Early observations on the relation of cadmium to other metals are indicated in connection with zinc. A. P. Laurie found cadmium to be electronegative towards zinc in contact with a soln. of *sodium chloride.* J. Tafel, and J. Tafel and B. Emmert measured the difference of potential of cadmium against platinum in *sulphuric acid;* and J. C. Poggendorff measured the difference of potential of cadmium against bismuth, palladium, iron, mercury, and amalgamated cadmium in dil. sulphuric acid. A. P. Laurie measured the

difference of potential of zinc against platinum in soln. of *cadmium iodide and iodine ;* J. Regnauld, of cadmium against carbon in soln. of *potassium iodide and iodine ;* and F. Streintz, of cadmium against zinc, and copper in soln. of *cadmium nitrate ;* of cadmium against magnesium, zinc, tin, cobalt, copper, silver, mercury, and bismuth in soln. of *cadmium sulphate ;* of cadmium against zinc, and copper in soln. of *cadmium chloride.* C. R. A. Wright and C. Thompson, and F. M. G. Johnson and N. T. M. Wilsmore measured the difference of potential of cadmium against amalgamated zinc, magnesium, aluminium, copper, silver, mercury, and lead, in soln. of the nitrate, sulphate, chloride, bromide, or iodide. L. Kahlenberg measured the difference of potential of cadmium against zinc, and silver in pyridine soln. of cadmium nitrate. E. F. Herroun, of cadmium in a soln. of cadmium sulphate or chloride against tin in a soln. of *stannous chloride.*

The **heat of ionization** of cadmium per valence is given by W. Ostwald [19] as 8300 cals.; H. Jahn gives 16·12 Cals. for $Cd^{\cdot\cdot}$-ions. The **transport numbers** of cadmium ions have been measured by K. Drucker, F. Kohlrausch, F. J. Wershoven, O. Grotrian, W. Hittorf, J. W. McBain, G. Kümmel, V. Gordon, R. Lenz, G. Carrara, E. Rieger, B. D. Steele, etc. The **velocities of the ions,** V, have been measured by F. Kohlrausch, and A. E. Garrett. The velocities, V, in mm. per sec. of the cation of soln. containing n mols of cadmium sulphate per litre are :

n	0·1	0·04	0·02	0·01	0·005	0·0025
V	0·023	0·029	0·026	0·036	0·045	0·051

R. Lenz, W. Hampe, W. Hittorf and F. J. Wershoven investigated the conductivity of alcoholic soln. W. P. Davey gave 0·95 A. for the **atomic radius** of the cadmium ion in cadmium sulphide, and 1·11 A. in the oxide. The **electrochemical equivalent** corresponds with the deposition of 2·0886 grms. of cadmium per ampère-hour.

The **decomposition voltages** of aq. soln. of many cadmium salts—sulphate, phosphate, cyanide, chloride, nitrate, and complex salts—have been determined by many investigators [20]—M. le Blanc, H. Freudenberg, H. E. Patten and W. R. Mott, J. E. Root, C. Coffetti and F. Förster, A. Brunner, A. Schweitzer, etc. C. C. Garrard investigated molten cadmium salts. P. A. Favre, and H. Jahn compared the thermal and electrical energy required for the decomposition of these salts. The electrolytic **solution pressure** of cadmium in aq. soln. has been investigated by C. R. A. Wright and C. Thompson,[21] F. Braun, W. Ostwald, B. Neumann, H. Jahn, O. Sackur, G. Carrara and L. d'Agostini, etc. The constant works out at approximately 10^7 atm. H. C. Jones and A. W. Smith estimate the soln. press. of zinc in alcohol to be approximately 10^8 times smaller than in water. The **overvoltage** of hydrogen on cadmium electrodes in N-H_2SO_4 is approximately 0·48 volt. The subject has been investigated by J. Tafel,[22] W. A. Caspari, N. R. Dhar, E. Müller, A. Coehn and Y. Osaka, etc. The **polarization** of cadmium electrodes has been investigated by H. Jahn, M. le Blanc, A. Coehn and Y. Osaka, O. H. Weber, etc. J. S. van der Lingen studied the **electrodeless discharge** in cadmium vapour. B. Pogany sought for the **Faraday effect**—the rotation of the plane of polarization in a magnetic field—with thin films of cadmium. According to H. Schönn, cadmium becomes passive in contact with platinum in nitric acid, of sp. gr. 1·47, but not in dil. nitric acid. U. Sborgi and P. Marchetti have studied the anodic behaviour of cadmium in a sat. soln. of lithium chloride in acetone. The **electrolytic valve-action** of cadmium has been discussed by A. Günther-Schulze,[23] and W. Holtz in aq. salt soln.

The **electric discharge** between cadmium electrodes has been studied by C. E. Guye and A. Bron,[24] F. Müller, A. Pospieloff, and C. A. Skinner. The potential gradient of the arc was investigated by V. L. Chrisler; the **disintegration of cadmium electrodes** by W. Crookes, G. Grandquist, and V. Kohlschütter and R. Müller. K. Honda found that the **magnetic susceptibility** of cadmium at 18° is $-0{\cdot}17\times10^{-6}$ units of mass, and at 700°, $-0{\cdot}15\times10^{-6}$ units.

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§ 6. The Chemical Properties of Zinc and Cadmium

G. Williams [1] found that zinc can occlude 38 times its vol. of **hydrogen**; but A. Sieverts, J. Hagenacker, and W. Krumbhaar stated that no hydrogen is dissolved by molten zinc; and G. Neumann and F. Streintz, that electrolytic zinc occludes but traces of hydrogen. W. Heald found zinc and cadmium films do absorb some hydrogen gas. A. Fowler and H. Payn obtained spectral indications which could be interpreted by the assumption that *cadmium hydride* is formed. B. Delachanal found that when 100 grms. of ordinary zinc are heated in an evacuated porcelain tube, the **occluded gas** contains 18·15 c.c. of hydrogen, 1·65 c.c. of carbon monoxide, and 0·50 c.c. of carbon dioxide. M. Guichard noted that zinc after five sublimations under reduced press. gives off 2 c.c. of occluded gas per 100 grms. of metal; and the occluded gas in cadmium, which has been purified by repeated sublimation, has a vap. press of approximately 0·01 mm. H. Pauli stated that the sp. gr. of zinc may fall from 6·52 to 3·5 owing to the occlusion of gas. C. A. Skinner obtained hydrogen by using freshly polished zinc as cathode in the helium discharge tube, and nitrogen, by using it in an evacuated discharge tube.

L. N. Vauquelin believed that he had prepared *zinc hydride* or *zincuretted hydrogen* by igniting zinc blende with one-fourth of its wt. of charcoal. He also described the properties of the supposed compound, *e.g.* it was said to be lighter than air, and heavier than hydrogen; to burn in air with a yellowish-white flame producing zinc oxide, and a small quantity of metallic zinc; and to explode when mixed with chlorine and ignited to produce zinc chloride and hydrogen chloride. It was further stated that it is not decomposed by nitric acid, or by easily reduced metallic salts. It is not absorbed by water, and does not combine with the bases. E. W. von Siemens and J. G. Halske, and A. R. Leeds believed in the existence of a gaseous zinc hydride; the latter regarded the blue colour of the flame of hydrogen obtained from zinc as evidence of the existence of a gaseous zinc hydride. R. L. Ruhland believed that he had obtained a solid zinc hydride by the electrolysis of zinc amalgam. C. A. Cameron denied that any gaseous zinc hydride is formed during the action of dil. acids on zinc, or the action of hydrogen sulphide on zinc amalgam. F. Paneth and co-workers observed no sign of the formation of zinc hydride by the action of activated hydrogen.

According to F. Fischer and G. Iliovici, the electric sparking of cadmium under liquid **argon** produces a voluminous olive-green powder, which forms cadmium oxide when calcined in air; the powder is insoluble in water, soluble in cold dil. hydrochloric, phosphoric, or acetic acid; and it is thought to be a nitride. According to O. Sackur, the catalytic activity of the following metals on the combustion of hydrogen decreases in the order Ag, Pt, Cu, Pb, Zn, Ni, Sn, Fe, Cr, and their proneness to assume the passive state increases in the same order.

P. A. von Bonsdorff [2] and M. Traube proved that zinc or cadmium remains bright in dry **oxygen,** or in dry **air** at ordinary temp., but if moisture be present, the hydroxide is formed, and if the air contains carbon dioxide as well, some basic carbonate is produced as a compact tenacious grey film which impedes the oxidation of the subjacent metal, and is thus unlike iron rust, which accelerates the oxidation of the subjacent metal. F. Stromeyer also stated that cadmium is tarnished by exposure to moist air, but if the air be free from carbon dioxide, the metal is not attacked. W. W. Coblentz found a polished cadmium plate was rendered matt by two days' exposure to air. When the surface of molten zinc is exposed to the air, it is speedily covered by a grey film, which is renewed as fast as it is removed, so that by repeated stirring the whole may be converted into a grey powder—*vide infra* zinc suboxide. According to J. F. Daniell, zinc takes fire in air at about 505°, and

it burns with a bluish-white flame, forming zinc oxide, *q.v.* O. Ohmann found zinc wool burns with a very brilliant flame when lighted with a Bunsen's burner. F. Stromeyer also noted that cadmium readily burns when heated in air, and W. Manchot detected the formation of some cadmium peroxide in the products of the reaction. J. Rothe and F. W. Hinrichsen found that moist air has no perceptible action on cast zinc after 6 hrs.' exposure, and a slight film appears after 8 hrs.' exposure. Moist air containing 5 per cent. of carbon dioxide, by vol., exerts no perceptible action in 6 hrs., but after 24 hrs. a white film is visible ; the action is rather more pronounced if a greater proportion of carbon dioxide is present. If the air contains sulphur dioxide in place of carbon dioxide, the attack is faster, and it can be detected after half an hour's exposure of zinc to moist air with 5 vol. per cent. of sulphur dioxide. E. Jordis and W. Rosenhaupt observed that the action of oxygen on zinc begins about 180° ; and below 200°, moist oxygen acts more slowly, and above 200° more rapidly than the dried gas ; at 300° the oxidation is twice as rapid with moist oxygen as it is with the dry gas, and the difference becomes less marked as the temp. rises. The effects are due not to the reaction itself, but rather to a kind of surface film which is developed. At a temp. below 150°, oxidation virtually ceases in dry oxygen as soon as the surface film is formed, while above 150°, the reaction continues. An oxidizable surface may be the result of (*a*) the soln. of oxygen in the metal ; (*b*) the diffusion of the oxygen through the layer of oxide which may dissolve the oxygen or be merely porous to it ; (*c*) the alternate formation of low and high oxides ; or (*d*) the layer of oxide scaling off from the metal. P. Schwalbe studied the combustion of zinc in compressed oxygen and compressed air. N. B. Pilling and R. E. Bedworth found that at 400°, zinc oxidizes slowly in dry oxygen forming a milk-white film of oxide. G. Tammann and W. Köster studied the speed of formation of films on zinc and cadmium in heated air or oxygen.

Zinc dust can inflame in moist air owing to rapid oxidation. W. Manchot found that the temp. at which air and **ozone** act on zinc or cadmium are close together, but ozone acts more energetically. C. Engler and W. Wild found that clean and moist zinc filings react with ozone, forming a pale cloud of zinc oxide. G. C. Schmidt examined the action of canal rays on gases in the presence of zinc, etc. According to J. Priestley, A. von Humboldt, J. W. Ritter, W. Wilson, and J. C. L. Reinhold, zinc is more rapidly attacked if it be in contact with a piece of copper. M. Müller also noted that zinc tubes in contact with a copper roof were rapidly corroded. F. Mylius and R. Funk observed a peculiar corrosion of zinc anodes during the electrolysis of soln. of zinc sulphate ; and J. H. Aberson found that zinc is gradually dissolved from brass. According to P. A. von Bonsdorff, if two metals are placed, not in contact with one another, under a bell-jar containing air, and closed at the bottom with a water-seal, the more oxidizable metal is alone bedewed, and therefore oxidized ; for example, arsenic or lead placed in a moist atm. near copper or silver. Again, if a piece of lead be placed under the receiver near a piece of zinc, the last-named metal remains bright while the lead is tarnished. The contrary effect is produced if the metals are in contact—thus, if copper is placed in contact with silver, the moisture condenses only on the surface of the last-named metal—*vide* sacrificial metals—**1.** 16, 3.

M. Pettenkofer and A. Bolzano studied the corrosive action of atm. air on zinc. The former found that a zinc roof in München oxidized 8·381 grms. per sq. ft. (Bavarian) in 27 years—the film of oxide was about 0·1 mm. thick, and had the composition $5ZnO.4CO_2.8H_2O$. G. T. Moody suspended strips of thin sheet zinc in a muslin bag under the shelter of a north wall, and exposed to the full effects of the atm. for 5 months ; the semi-crystalline scale which was formed had a composition agreeing closely with $ZnCO_3.3Zn(OH)_2$. G. T. Moody regards this as evidence that the atm. corrosion of zinc is not due to the direct oxidation of the metal, but to an interaction with carbonic acid. W. R. Dunstan regarded the atm. oxidation of zinc as a complex process in which

as shown by M. Traube, W. Smith, and H. T. Barnes and G. W. Shearer, hydrogen peroxide is formed as an intermediate product—$Zn+O_2+2H_2O=Zn(OH)_2+H_2O_2$, followed by $Zn+H_2O_2=Zn(OH)_2$—which can be detected during the process of oxidation. W. Merckens arranged the metals in the order: Mg, Al, Zn, Cd, Ni, Co, Pb, according to their power of forming hydrogen peroxide during their oxidation. Any reagent which prevents the formation of hydrogen peroxide prevents the oxidation of the zinc. Any carbonate which may be present in the rust is a secondary effect due to the action of carbon dioxide on the zinc hydroxide. G. T. Moody found that commercial **hydrogen peroxide** rapidly transforms zinc into the hydroxide while 30 per cent. hydrogen peroxide has scarcely any action on the metal. W. R. Hodgkinson and A. H. Coote noted that an ammoniacal soln. of hydrogen peroxide rapidly dissolves zinc.

According to J. J. Berzelius, and W. van Rijn, when zinc filings are moistened with **water** and exposed to the air, they acquire a dark colour, increase in vol., and hydrogen gas is evolved with a visible effervescence, while a grey oxide is formed. Zinc submerged in water in contact with air freed from carbon dioxide is soon covered by a film of oxide. F. Stromeyer remarked that cadmium does not decompose water at ordinary temp.; and P. A. von Bonsdorff found that cadmium becomes covered with hydrated oxide when immersed in water exposed to air free from carbon dioxide, but if the latter gas be present, the deposit contains some carbonate. According to P. A. von Bonsdorff and P. H. Boutigny, zinc does not attack purified water at ordinary temp.; and the metal together with water, freed from air by boiling, may be sealed up in a glass tube and kept for a year without any diminution in the brightness of the metal. C. F. Schönbein showed that hydrogen peroxide is formed when zinc, cadmium, lead, or copper is in contact with water and air. M. T. Mengarini found that when in contact with distilled water, zinc gradually yielded a colloidal soln. of zinc or zinc oxide or hydroxide, which can be detected by the ultramicroscope. J. Davy stated that zinc does not decompose boiling purified water even if the zinc be in contact with copper, but if the water contains a salt in soln., reaction does occur. On the contrary, J. J. Berzelius, J. Thomsen, J. P. Cooke and W. Smith maintained that boiling water is decomposed by zinc; and J. Percy found that commercial sheet zinc is slowly decomposed by water just below 100° and from which air had previously been expelled by boiling; the evolution of hydrogen decreased after one or two hrs. The contradictions are due to inattention to the degree of purity of the zinc. L. l'Hôte showed that highly purified zinc does not give hydrogen when boiled for a long time with water, but if 0·03 to 0·05 per cent. of iron or a trace of arsenic or antimony is present, zinc does decompose boiling water. B. Roux also showed that the influence of water on zinc is dependent on the nature of the water. When the metal is boiled with water in glass vessels, the alkali dissolved from the glass was shown by H. E. Davies to have an important influence on the results. L. B. G. de Morveau noted that rain-water does not attack zinc while spring-water does so, and numerous cases have been reported—by C. W. Heaton, F. Schwarz, T. Stevenson, T. L. Phipson, H. Struve, P. A. E. Richards, P. F. Frankland, M. E. Chevreul, O. Krug and M. Rautert, H. Fleck, H. W. Bettink and J. van Eyk, A. Wagner, J. Nessler, A. Brüning, M. Tergast, E. Hylius, F. Hundeshagen, J. L. Howe and J. L. Morrison, C. H. Ehrenfeld, etc.—where water which has passed through zinc pipes, or galvanized iron pipes, or been stored in zinc-lined tanks, is contaminated with a soluble compound of zinc. H. E. Davies found that water which had passed through a considerable length of galvanized iron-pipe contained 1·7 parts of zinc per 100,000 parts of water; C. W. Heaton, 6·41 grains per gallon; and F. P. Venable, 4·48 grains per gallon. A. Smetham mentioned a boiler deposit with 44 per cent. of zinc oxide. According to A. Siersch, zinc dissolves rapidly in soln. of alkali chlorides and sulphates; O. Aschan found that sea-water attacks zinc more rapidly than purified water, and F. C. Calvert and R. Johnson found that in one month 100 litres of sea-water dissolved 5·66 grms. per sq. metre of zinc, or 1·12 grms. per sq. metre of galvanized iron.

A. J. C. Snyders reported that hard well waters do not act on zinc, but soft-waters and rain-water containing ammonium salts do act on that metal. The solubility of zinc in natural waters is said to depend on the proportion which exists between the carbonates and phosphates, and the chlorides, sulphates, and nitrates, the most injurious salts of the latter class being the ammonium salts, then the chlorides of the alkaline earths, and the chlorides and sulphates of the alkalis. A. J. C. Snyders further stated that zinc decomposes saline soln., whether conc. or dil. without access of oxygen, evolving hydrogen and forming zinc oxide. From his experiments on the action of water and saline soln. on zinc, X. Rocques concluded that zinc is attacked very slowly by ordinary water and saline soln. in general, *i.e.* containing chlorides and bi-carbonates. If several metals are present the action is much more rapid. The maximum effect occurs in presence of oxygen. This is particularly the case at the surface of the reservoir where the metal is in contact with air and water by turns. H. E. Davies concluded that all kinds of water attack zinc in the presence of air, and that rain-water exerts least action; a moderate degree of hardness favours the action, while extreme hardness does not prevent the action. When the metal is covered by a film of the hydroxide, the action does not cease, although its speed is much reduced. When water containing zinc compounds is drunk, zinc is afterwards found in all the viscera.

W. Smith, and X. Rocques noted that the presence of ammonia or nitrogenous organic matter in water accelerates the attack. O. P. Watts and N. D. Whipple studied the corrosion of cadmium, zinc, and zinc amalgam by hydrochloric, nitric, chromic, sulphuric, perchloric, phosphoric, and acetic acids; by sodium hydroxide soln.; and by soln. of hydrogen peroxide; sodium nitrite and arsenate; ferric sulphate and chloride; potassium chlorate, dichromate, permanganate, nitrate, bromide, and iodide; and by mercuric chloride. They added that amalgamation protects zinc from acids because the discharge potential of hydrogen on mercury exceeds that on zinc. A. J. Hale and H. S. Foster examined the action of nitric, sulphuric, and hydrochloric acids; aq. ammonia; sodium hydroxide, chloride, and carbonate; and magnesium and calcium chlorides on zinc. According to L. Santi, A. Bringhenti, A. Wagner, and A. J. C. Snyders, zinc also dissolves in a soln. of **ammonium chloride.** M. Müller found that the reaction is faster if air be present. According to H. Ritthausen, a dil. or conc. soln. of purified ammonium chloride is not perceptibly decomposed by zinc either at ordinary temp. or when warmed, but if some cupric chloride or an acid or alkali is present, the soln. is decomposed. A. Bringhenti found the reaction with a soln. of **ammonium fluoride** to be very vigorous. J. B. Davies, and J. E. Lorin, also showed that soln. of ammonium salts favour the dissolution of zinc. W. Smith, and A. J. Hale and H. S. Foster observed that a soln. of **sodium chloride** dissolves zinc, A. Siersch found that hydrogen is evolved, and a soln. of sodium zinc chloride and a deposit of zinc oxide formed. A. Krefting exposed a mixture of sodium chloride and zinc filings to moist air and obtained a mixture of zinc hydroxide with basic chloride and carbonate. C. H. Crowe studied the action of the chlorides, sulphates, and nitrates of potassium, sodium, and magnesium and found that while zinc was attacked by the nitrates and sulphates, it was scarcely affected by the chlorides. A. Vogel stated that when zinc or cadmium, under water containing $\frac{1}{300}$th part of **potassium hydroxide,** is exposed to air, the metal turns grey, and forms shining laminæ of zinc carbonate, but no zinc dissolves in the water. A. Langlois also studied this reaction. As shown by A. Langlois, A. J. Hale and H. S. Foster, A. Vogel, A. Destrem, L. de Boisbaudran, J. A. Poumarède, G. Bischof, and J. M. F. de Lassone, zinc dissolves slowly in soln. of the **alkali hydroxides** liberating hydrogen, and forming a soluble alkali zincate; the presence of the more electro-negative metals accelerates the process of dissolution, thus F. F. Runge found the speed of soln. is greater when the zinc is in contact with platinum, and still more so when in contact with iron. According to A. J. C. Snyders, the greater solvent action of saline water is due to the increased solubility of the zinc oxide in the liquid. Thus, C. Matignon and G. Desplantes stated that the oxidation of cadmium

or zinc by water in the presence of oxygen is not accelerated appreciably by ammonia, but that the presence of ammonia favours the reaction by dissolving the product of the oxidation. R. Ihle found that zinc is rapidly oxidized in aerated water or salt soln., and that the reaction is retarded by hydroxides, carbonates, phosphates, borates, and nitrites, but accelerated by chlorides, bromides, chlorates, nitrates, sulphates, etc. According to H. V. Regnault, when water vapour is passed over zinc at a dull red heat, hydrogen gas is liberated, and small crystals of oxide are deposited on the metal. H. St. C. Deville also studied the reaction: $Zn+2H_2O \rightleftharpoons Zn(OH)_2+H_2$. H. V. Regnault found that cadmium acts in a similar manner.

Zinc unites energetically with most of the metalloids; and the properties of cadmium closely resemble those of zinc, but the chemical energy of cadmium is the smaller. For example, the thermal values of the reactions with zinc are usually greater than those with cadmium; and zinc will precipitate cadmium from soln. of its salts, and this property has been utilized in separating the two metals—*vide* cadmium. According to H. Moissan,[3] **fluorine** reacts with warm powdered zinc with incandescence. According to H. Davy, zinc-foil at ordinary temp. inflames in **chlorine**; and T. Andrews stated that although zinc combines energetically with moist chlorine, "perfectly dry chlorine has no action whatever at ordinary temp., . . . and the same remark applies to the action of dry bromine in contact with the dry metals." R. Cowper also found that neither the dry gas nor liquid chlorine attacks zinc or cadmium at ordinary temp. C. Löwig found that zinc does not combine with **bromine** even when the bromine is dropped on the heated metal, although J. B. Berthemot noted that the two elements react at a red heat. A. J. Balard found that zinc readily dissolves in bromine water; J. L. Gay Lussac found that **iodine** and zinc readily combine with the evolution of a small amount of heat. The heat of the reaction between the halogens and zinc is greater, the smaller the at. wt. of the halogen. A. Schükareff represented the speeds of the reactions between an aq. soln. and one of the halogens and zinc by the formula $\log (C/C')=kt$, where C and C' represent conc., and t the time. The quantities of halogen reacting during a given time in equally conc. soln. on equal surfaces of the metal are equal; or, in other words, the quantities of metal reacting in a given time at equal or equivalent conc. are proportional to the at. wt. of the metal, and inversely proportional to its valency in the compound formed. G. Tammann and W. Köster studied the formation of films on zinc exposed to chlorine or bromine mixed with air. G. Tammann studied the character of the film produced when zinc or cadmium is exposed to the vapour of iodine at ordinary temp.

The gaseous **hydrogen halides** and their aq. soln. readily attack zinc with the evolution of hydrogen, and the formation of the corresponding zinc halide. N. N. Beketoff [4] found that when dry cadmium is heated in an atm. of dry hydrogen chloride at 440°, about 98 per cent. of the gas is decomposed: $Cd+2HCl \rightleftharpoons CdCl_2+H_2$. From the time of C. F. Wenzel's study of the kinetics of that class of heterogeneous reactions represented by the dissolution of zinc in various acids, in 1777, a great deal of the work has been done with this metal. The subject has been investigated by T. Ericson-Aurén and W. Palmaer, A. J. Hale and H. S. Foster, E. Brunner, etc. These reactions are more sensitive to disturbing influences than those which take place in homogeneous systems. As shown by F. C. Calvert and R. Johnson, the speed of the reaction is influenced by variations in the rugosity of the surface of the dissolving metal: they stated that

> Cubes, which had been made of the same zinc but at different times, were acted upon more or less by the same acid when placed under the same circumstances; and these observations gradually led us to the discovery of a curious fact, viz., that a perfectly clean surface of zinc will become after a few days sufficiently oxidized by contact with air to modify in a very marked degree the action of sulphuric acid upon it. Thus, if a cube of zinc recently filed is placed in sulphuric acid diluted with nine equivalents of water, the action may be considered as nil; whilst if the same cube be gently heated in contact with air and allowed to cool, and be then placed in the same strength of acid, the attack is marked.

Hence, the roughness of the surface and not oxidation is the *vera causa* of the increased velocity, for superficial oxidation could not exert more than a momentary influence owing to the solubility of the oxide in the acid. The speed of the action is also modified by the local rise of temp. due to chemical action, by the rate of diffusion of the products of the reaction in the acid liquid; by the disengagement of gas-bubbles from the surface of the metal; by the impurities associated with the metal; and, as shown by G. Tammann, W. Nernst, and F. Kunschert, E. Brunner, etc., by the difference of potential between the metal and the acid; and by the conductivity of the soln. K. Jablczynsky concluded that the velocity of dissolution of a solid with a perfectly smooth surface increases proportionally with the *velocity of stirring*, and if the surface of the solid is not smooth, the increase of the velocity constant is slower than the increase of the velocity of stirring, and the more so the rougher the surface. H. J. Prins found the rate of dissolution of zinc in many acids is accelerated by the presence of nitrobenzene, or benzaldehyde; and A. Sieverts and P. Lueg, that the presence of a trace of nicotine, quinine, or of α- or β-naphthoquinoline greatly retarded the activity of hydrochloric acid.

Highly purified zinc was shown by A. A. de la Rive to be scarcely affected by the acid. The most rapid action occurred when commercial zinc was treated with about 30 per cent. sulphuric acid. He added known quantities of tin, lead, copper, and iron, respectively, to molten redistilled zinc, and found that the rates of action of the products with sulphuric acid soln. were greater than the rate of action of redistilled zinc. Finally, he proved that the soln. of sulphuric acid which showed maximum electrical conductivity interacted most rapidly with commercial zinc, and with redistilled zinc to which a few per cent. of iron had been added. He concluded that the interaction between pure zinc and dil. sulphuric acid is probably a direct chemical change, but that with ordinary commercial zinc the action is chiefly electrochemical. M. Faraday also proved that a plate of amalgamated zinc remained unchanged in sulphuric acid, to which 30 parts of water had been added, while a similar plate in the same acid, and in contact with a platinum plate, was rapidly dissolved. N. A. E. Millon added that the more pure the zinc, the slower the action of the acid, but the purified metal readily dissolves if it be in contact with platinum or some other electronegative metal. In illustration, with $\frac{1}{10}$-normal hydrochloric acid 39 c.c. of gas were evolved by the dissolution of zinc for 300 minutes under conditions where 78 c.c. were evolved when the zinc was in contact with platinum. In 600 minutes the numbers were respectively 68·4 c.c. and 103·3 c.c. H. C. Reynolds and W. Ramsay found highly purified zinc to be nearly unacted upon by hydrochloric or sulphuric acid. Hence, the reaction between zinc and dil. sulphuric acid is probably electrolytic, and dependent on the formation of local galvanic couples on the surface of the dissolving metal. It has therefore been inferred that pure zinc is insoluble in pure acid, and that if a third substance be present in metal or acid, dissolution takes place by the formation of an electrical circuit. Purified cadmium behaves similarly. The *reversed electrolysis* theory of chemical action developed by H. E. Armstrong assumes that two substances will react only in the presence of certain impurities; pure substances do not interact. Before chemical action can occur, a conducting system must be established between the two interacting substances and the third component. J. M. Weeren believed that the resistance offered by purified cadmium or zinc to the acid is due to the immediate formation of a film of hydrogen which shields the metal from the acid. J. C. d'Almeida, and F. Pallinger observed that the hydrogen is liberated from the impurities in metallic zinc when the acid has free access to the metal. A. Coehn and W. Caspari stated that the resistance which purified zinc offers to attack by acids depends on the high overvoltage of hydrogen and zinc, which is lowered from 0·70 volt to 0·23 volt when the zinc is in contact with copper, and to 0·15 volt when the zinc is in contact with silver, and the zinc then readily dissolves. C. Düsing also found zinc with 3–15 per cent. of iron is very resistant, and this alloy has therefore been recommended as anode in the electrolysis of soln.

of zinc salts. F. Novak found that by raising the proportion of cadmium in plumbiferous zinc, the velocity of attack is reduced, and the period of induction is extended.

W. Spring and E. van Aubel measured the speed of dissolution of zinc in sulphuric acid, **hydrochloric acid, hydrobromic acid,** and **hydriodic acid.** They found that the rate of dissolution is proportional to the conc. of the acid. F. Zecchini also found that the velocity of the reaction is approximately the same with $\frac{1}{10}N$-soln. of hydrochloric and sulphuric acids at ordinary temp., and that the speed of attack increases proportionally with the conc. of the acid but faster with hydrochloric than with sulphuric acid. E. Divers and T. Shimidzu concluded from their observations on the rate of dissolution of zinc in sulphuric and nitric acids that other circumstances being equal the time taken to neutralize a given quantity of acid, or to complete some other chemical action upon it, is directly proportional to the dilution of the acid, and inversely as the area of contact between the metal and the soln. It is independent of the quantity of the acid. W. Ostwald observed that the relative affinity of hydrochloric and sulphuric acids on zinc, increases as the conc. decreases. According to W. Spring and E. van Aubel, the effect of *temperature* on the speed of dissolution of zinc in hydrochloric acid is shown by a curve asymptotic to the temp. axis, and that the isothermal curves for 5, 10, and 15 per cent. hydrochloric acid, at 15°, 35°, and 55°, all converge to zero, corresponding with −60° to −70°. T. Ericson-Aurén found that with very dil. acids, the speed of dissolution is scarcely affected by the temp. F. Zecchini found the effect of temp. is less with hydrochloric acid than with sulphuric acid ; a rise from 10° to 50° raises the velocity with 0·1 to 0·5N-H_2SO_4 by 50 to 150 per cent. L. P. Cailletet, M. Berthelot, J. Babinet and P. A. Favre, and J. W. Gunning noted the decrease in the solubility of zinc in acids under *pressure—vide* **1.** 7, 5. W. Hankel studied the *electrical phenomena* associated with the action of acids on zinc ; and G. Berndt found that the rate of dissolution of zinc in hydrochloric acid is not influenced by a *magnetic field.* Owing to differences in the crystalline structure of the metal, rolled zinc is more readily attacked by dil. acids than is cast zinc, and P. A. Bolley maintained that zinc cast at a low temp. is much more rapidly attacked by acids than when the metal is cast at a red heat. The subject has been investigated by M. Barrett, K. Begemann, and C. F. Rammelsberg.

E. J. Mills and W. J. Mackey noted the *period of induction* in the dissolution of metals in acids—*vide* **1.** 7, 4. M. Centnerszwer assumed that the period of induction with zinc is due to the metal passing from a passive to an active state—*vide* passive zinc. W. Spring and E. van Aubel divided the reaction into three stages : The first is a period of induction which they suppose to be abnormal, and is dependent on the production of an indefinitely large number of minute galvanic couples on the surface of the metal ; in the second stage the activity attains its maximum value ; and in the third stage, this activity decreases as the conc. of the acid is diminished. A. J. J. van de Velde found that for all conc. of hydrochloric acid, the period of induction with hydrochloric acid is longer than with sulphuric acid, and with the latter it is longer than with nitric acid ; he also found that the period of induction is abbreviated in the presence of cupric salts ; and that the activity of the acid is proportional to the conc. of the hydrogen ions. A. Merget showed that zinc on which any metal of the last three groups of Mendeléeff's table has been deposited is attacked by nitric acid only on the uncovered portions, while, on the contrary, sulphuric, hydrochloric, or acetic acid attacks only the covered portions. C. Gourdon found that zinc partly covered with a thin layer of precipitated platinum is attacked and dissolved by sulphuric acid dil. with 7000 times its vol. of water. With gold it is attacked by an acid dil. with 5000 parts of water ; copper requires an acid dil. with 4000 vols., silver 3500 vols., tin 1500 vols., antimony 700 vols., bismuth 500 vols., and lead 400 vols. The action is irregular with mercury, the spot gradually enlarging, and the zinc being dissolved only at the edges of the spot. The arsenites, arsenates, and antimonates also give spots which promote the soln. of the zinc, but the action is less

energetic. Deposits of cobalt, nickel, and iron, on the contrary, are comparable with those of platinum in their action, indeed cobalt causes the dissolution of the zinc by sulphuric acid dil. with 10,000 times its vol. of water. Salts of the same base, but with different acids, yield deposits which do not behave in the same way, the chlorides giving deposits which are more active than those produced by the sulphates, which in their turn excel those of the corresponding nitrates. Moreover, salts rendered slightly alkaline by the addition of ammonia give a more active deposit than the salts themselves; ferrous sulphate, for instance, produced no deposit by itself, but on adding ammonia a very active one is formed. Zinc thus covered with a metallic deposit is also readily attacked by alkalis.

According to F. Zecchini, the addition of zinc sulphate lowers the rate of the attack on zinc by sulphuric acid, and the addition of zinc chloride to hydrochloric acid at first decreases and then increases the speed of attack. J. Ball studied the effect of soluble sulphates on the speed of attack by sulphuric acid, and of soluble chlorides on the speed of attack by hydrochloric acid. The relative maximum velocities with sulphates and sulphuric acid with the velocity without any addition, taken as unity, are :

	Mg	Al	Cr	Mn	Fe	Ag	Co	Cu	Ni
Sulphates . .	0·98	1·02	1·66	2·06	2·34	9·36	18·09	21·7	37·87

Here, the effects with the first two are within the limits of experimental error, and these salts may be regarded as having no influence. The other salts accelerate the attack. Similarly with chlorides and hydrochloric acid :

	Mn	Pb	Sn	Cu	Co	Au	Pt	Ni
Chlorides . .	1·62	3·15	5·07	10·96	30·68	38·90	42·19	45·48

This subject has also been studied by F. Selmi, who found that the reaction between zinc and sulphuric acid is accelerated by small additions of manganese, magnesium, or iron sulphate, but not much affected by alkali or aluminium sulphate. G. Lunge observed that the activity of hydrochloric or sulphuric acid is lessened by admixture with gum, glycerol, or lampblack. F. Zecchini found that a soln. of hydrogen chloride in methyl, ethyl, or amyl alcohol, in acetone, or in aq. acetone attacks zinc, and the action of the ethereal soln., is most vigorous in spite of the insignificant ionization of the acid in soln. L. Kahlenberg, and H. E. Patten have studied the action of soln. of hydrogen chloride in benzene, and found a slow reaction which is accelerated by the addition of a little water. W. G. Falk and C. E. Waters found that a zinc rod wound with platinum is attacked by a soln. of hydrogen chloride in benzene, more slowly than a rod of purified zinc. H. E. Patten found the metal —zinc or cadmium—is only slightly attacked by a soln. of hydrogen chloride in chloroform, or arsenic trichloride, or carbon tetrachloride; but a marked corrosion occurs in benzene soln. L. Kahlenberg and H. Schlundt found a soln. of hydrogen chloride in liquid hydrogen cyanide attacks zinc.

The action of zinc on soln. of various **chlorides** has been already discussed. B. D. Steele found that when a soln. of **potassium iodide** is electrolyzed with a zinc anode, iodine is not set free, and the soln. becomes yellow, probably owing to the formation of zinc iodide. F. von Lerch studied the action of zinc on a hydrochloric acid soln. of **thorium X.** A. Terreil found zinc reacts explosively when heated with **manganese chloride;** R. Lorenz said that cadmium dissolves in molten **cadmium chloride;** N. N. Beketoff reported that a stream of hydrogen and zinc vapour attacks **barium chloride** superficially; O. Ruff, F. Eisner, and W. Heller found zinc rapidly attacks **tungsten hexafluoride,** especially if it contains some hydrogen fluoride, and hot or moist **tungsten oxytetrafluoride,** WOF_4, is also attacked; further, O. Ruff and H. Graf noted that heated **arsenic pentafluoride** acts on zinc, forming arsenic and zinc fluoride. J. H. Gladstone and A. Tribe found that zinc decomposes water in the presence of **aluminium iodide.**

According to A. D. White,[5] cadmium is not attacked by an aq. soln. of **bleaching powder,** and zinc is acted on only to a slight extent "because of the presence of

arsenic" ; H. P. Pearson also found a very slight action at first, but at the end of a fortnight some zinc oxide was formed, which increased to a powdery deposit at the end of six months. W. S. Hendrixson studied the action of zinc and cadmium on **chloric acid** (*q.v.*). A. L. Voege found that zinc cathodes favoured the electrolytic reduction of **potassium chlorate ;** and K. Weger found that in sulphuric or acetic acid soln. of chlorates a film of a basic salt is formed on the electrode, and this acts like a porous diaphragm. A. F. de Fourcroy and L. N. Vauquelin found that a mixture of powdered zinc and an oxidizing agent like potassium chlorate, detonates by percussion. G. Pellagri found that zinc powder reduces **potassium iodate** incompletely ; the reaction is complete with a zinc-copper couple.

Zinc has a strong affinity for **sulphur,** and W. Spring,[6] and L. Franck found that under a press. of 6500 atm. cadmium or zinc and sulphur unite to form the sulphide. C. Friedel, and E. Jannettaz question Spring's conclusion—*vide* **1**. 14, 18. E. Schwarz showed that the reaction between sulphur and a mass of the metal proceeds with difficulty because a protective layer of sulphide is formed ; on the other hand, a mixture of powdered zinc and sulphur reacts with explosive violence when warmed. The reaction between zinc and **selenium** or **tellurium** is accompanied by incandescence. Cadmium behaves similarly, but the reaction is not so vigorous. Zinc is attacked by **hydrogen sulphide** at ordinary temp., and a layer of sulphide is formed which protects the metal from further attack ; when heated in a stream of hydrogen sulphide the attack is vigorous. G. Tammann and W. Köster studied the formation of films on zinc and cadmium exposed to hydrogen sulphide. R. Lorenz prepared crystals of wurtzite is this way. E. Schwarz found **carbon disulphide** is reduced by powdered zinc, forming, with incandescence, zinc sulphide and carbon. P. Nicolardot found that zinc and cadmium are only slightly attacked by **sulphur chloride,** S_2Cl_2, and only after a prolonged action at as high a temp. as possible ; F. Wöhler also noted the slow attack of zinc by sulphur chloride. E. Fromm found that a soln. of **sulphuryl chloride,** SO_2Cl_2, in absolute ether, forms zinc chloride, sulphur dioxide, or zinc hyposulphite. P. Schutzenberger found that zinc dissolves without the evolution of gas in an aq. soln. of **sulphur dioxide,** forming zinc hyposulphite, ZnS_2O_4 ; and A. Nabl obtained a similar product by using an alcoholic soln. P. Schweitzer found that with cadmium and sulphurous acid, the liquid first becomes yellow, then clear, then dark, and sulphur and cadmium sulphide are precipitated ; when the mixture is boiled in the presence of hydrochloric acid, cadmium sulphide is precipitated at once. Among the products of the reaction, after a sufficiently long period, were cadmium sulphate, sulphite, thiosulphate, trithionate, and sulphide. After filtration and washing the precipitate contained only cadmium sulphide. Similar products were obtained with zinc. M. Berthelot also studied the action of sulphurous acid on cadmium, and found that in the presence of sulphuric or hydrochloric acid, cadmium sulphide and sulphur are formed ; C. Geitner found that under press., zinc and an aq. soln. of sulphur dioxide form zinc sulphate and sulphide, and free sulphur. J. Uhl also noted the formation of a sulphide as well as sulphate and sulphite when zinc or cadmium is heated in a stream of sulphur dioxide. M. Prud'homme found that with a soln. of **ammonium sulphite,** zinc forms zinc diammino-sulphate and ammonium hyposulphite. The corresponding reaction with **sodium sulphite,** and with **sodium hydrosulphite,** has been studied by R. von Wagner, and E. Berglund. F. Faktor said that cadmium colours yellow a boiling soln. of **sodium thiosulphate.**

The action of zinc and cadmium on **sulphuric acid** has been discussed generally in connection with its action on hydrochloric acid. The metal readily dissolves in dil. sulphuric acid, but, as shown by W. R. Grove,[7] and J. C. d'Almeida, amalgamated zinc is not attacked by this acid. P. B. Ganguly and B. C. Banerji found that rods of cadmium or zinc, partially immersed in the dil. acid, are most vigorously attacked near the surface of the liquid. A. Ditte found that at a low temp., dil. sulphuric acid and zinc furnish hydrogen and hydrogen sulphide, and some sulphur (soluble in carbon disulphide) ; at a higher temp. and with conc. acid, some sulphur

dioxide is formed. M. Berthelot found that 0·5 grm. of cadmium with 2 c.c. of sulphuric acid in a sealed tube at ordinary temp. developed 0·2 c.c. of hydrogen at ordinary temp., and at 100°, 3·5 grms., cadmium sulphate were also produced. At 160°, no hydrogen is formed, but only sulphur dioxide, and this the more the higher the temp. of the reaction. According to M. M. P. Muir and C. E. Robbs, conc. sulphuric acid, $7H_2SO_4+2H_2O$, exerts no action on zinc until a high temp. is reached, and that the gaseous product of the action which then occurs is sulphur dioxide, accompanied by separation of a little sulphur; $7H_2SO_4$, $4H_2O$ acts in a similar manner, but more sulphur separates; with $7H_2SO_4$, $6H_2O$, sulphur is no longer produced, but only hydrogen sulphide; as the acid is made more dil., the action commences at lower temp. with evolution of hydrogen and traces of hydrogen sulphide, or of hydrogen alone; the quantity of hydrogen sulphide is increased by rise of temp., but it is not accompanied by sulphur dioxide or sulphur. M. M. P. Muir and R. H. Adie added further that the dependence of the production of hydrogen sulphide and sulphur dioxide on the temp. and conc. of the acid indicates that the formation of these gases is not to be ascribed to the reducing action of nascent hydrogen on the acid. This is confirmed by the observation that variations in the mass of zinc employed and the quantity of hydrogen produced in a given time, do not exert any marked or regular effect on the nature of the change; and further confirmed by the observations that an acid of conc. $H_2SO_4+2H_2O$ with commercial zinc gives very little sulphur dioxide or hydrogen sulphide at 100°, while both gases are produced freely at 165°, and a large proportion of hydrogen sulphide at 180°; with purified zinc both gases are produced at 165°. If the gases were secondary products of the reduction of sulphuric acid by the hydrogen evolved in the primary change, it might be expected that both gases would be formed as freely with purified as with commercial zinc. It is probable that the interaction between approximately pure zinc and acid is chiefly a direct chemical interaction, and that the products of the reactions with less pure zinc are largely due to the occurrence of secondary electrolytic changes. With pure, or almost pure, zinc and dil. acid (say $H_2SO_4.12$ to $15H_2O$), hydrogen and zinc sulphate are the only products of the reaction; with the same zinc and conc. acids (say $H_2SO_4.H_2O$ to H_2SO_4) the chief gaseous product is sulphur dioxide: and hydrogen sulphide is also produced at higher temp.; with sulphuric acid of intermediate conc. (say $H_2SO_4.2H_2O$) both compounds of sulphur are formed in considerable quantities at fairly high temp., *viz.* 160°.

The higher the degree of purity of the zinc, the smaller the proportion of sulphur dioxide to that of hydrogen sulphide at ordinary temp. whether the acid be dil. or conc. With an acid more dil. than $H_2SO_4+10H_2O$, hydrogen is almost the sole gaseous product even at temp. up to the b.p. of the acid. With purified zinc, at about 160°, the dil. of the acid is accompanied by a decrease in the proportion of sulphur dioxide and hydrogen sulphide produced, but with commercial zinc, the sulphur dioxide diminishes more than the hydrogen sulphide. The latter gas is always found with commercial zinc at dilutions down to $H_2SO_4+100H_2O$, and at temp. from 0° to the b.p. of the acid. Platinized zinc behaves very like commercial zinc. Sulphur is produced neither at low temp. nor with acids less conc. than $H_2SO_4+2H_2O$, and when sulphur is produced, sulphur dioxide and hydrogen sulphide are always formed. With purified zinc and sulphuric acid, there is scarcely any separation of sulphur; with platinized foil, on the other hand, sulphur is formed in large quantities. The sulphur can scarcely be a product of the interaction of sulphur dioxide and hydrogen sulphide, else it might be expected to generally accompany these gases; nor can it always be produced by the reducing action of the nascent hydrogen on either the sulphur dioxide or hydrogen sulphide, because these gases are so frequently found at moderate temp. unaccompanied by sulphur. The formation of sulphur can sometimes be traced to the mutual action of hydrogen sulphide and hot conc. sulphuric acid. This supposition would account for the preponderance of sulphur dioxide over hydrogen sulphide when the acid is

conc. and for the increase in the quantity of the latter gas as the acid becomes more dil.; for the hydrogen sulphide supposed to be formed when the acid is conc. would be decomposed by reacting with the hot acid, but would escape unchanged when the acid becomes more dil. The fact that the cessation in the production of sulphur is accompanied by a marked increase in the quantity of sulphuretted hydrogen in the reaction of platinized foil with conc. acids, is also in keeping with this supposition.

W. B. Hart, A. J. Hale and H. S. Foster, A. Sieverts and P. Lueg, and E. Brunner have also studied the reaction between zinc and sulphuric acid; and E. J. Mills and W. M. D. Mackey obtained a formula showing the effect of the conc. of the acid on the process. M. Barrett studied the state of aggregation of the zinc on the rate of dissolution in dil. sulphuric acid. F. Pullinger found that zinc with a perfectly smooth surface is not acted upon by dil. sulphuric acid which has been submitted to prolonged boiling. That pure zinc with a rough surface is readily acted upon, but in a less degree by acids which have been boiled than by those which have not. That oxidizing agents, such as electrolyzed sulphuric acid, hydrogen peroxide, and nitric acid, increase the rate of dissolution. That a reducing agent, such as hydriodic acid, almost entirely prevents dissolution, but that those containing sulphur, such as sulphur dioxide, are without effect. That, in all probability, *pure* dil. sulphuric acid would, at ordinary temp., be entirely without action upon metallic zinc, whether the surface of the latter were rough or smooth. F. Pullinger assumed that ordinary "pure" sulphuric acid probably contains a small quantity of some substance which is wholly or partly decomposed or driven off by boiling. This substance is not hydrogen sulphide nor sulphur dioxide, and it is not hyposulphurous acid, nor any of the acids contained in Wackenroder's soln. From the fact that oxidizing agents, such as hydrogen peroxide, nitric acid, and sulphuric acid which has been electrolyzed increase the velocity of dissolution, it is not improbable that the third substance is some lightly oxygenated compound. This view is borne out by the action of hydriodic acid, a reducing agent which very greatly retards the rate of dissolution of zinc. He assumed that this third substance is persulphuric acid which acts as a catalytic agent in the reaction between zinc and sulphuric acid, analogous with nitrous acid in the reaction between copper and nitric acid (*q.v.*).

L. Kahlenberg and H. Schlundt found that zinc is not attacked by a soln. of **sulphur trioxide** in liquid hydrogen cyanide, but that it is attacked by a soln. of **fuming sulphuric acid** in that menstruum. Zinc decomposes **selenic acid,** H_2SeO_4, and **molybdic acid,** H_2MoO_4. The action of soln. of **alkali sulphates, magnesium sulphate,** and of **ammonium sulphate** on zinc has been investigated by A. Bringhenti, A. J. C. Snyders, A. Wagner, and A. Krefting; the latter also studied the action of **sodium tungstate.** H. S. Rawdon and co-workers found the corrosion of annealed zinc by soln. of **zinc sulphate** is of an intercrystalline nature. A. R. Wahl studied the reduction of a soln. of **ferric sulphate** to ferrous sulphate by zinc; he did not detect the evolution of any hydrogen, and utilized the reaction for the evaluation of zinc dust. S. Sugden also made observations on this reaction. F. Muck claimed that with a conc. soln. of **ferrous sulphate,** hydrogen is evolved, and an ochre-yellow deposit is formed. J. Löwe found that granulated zinc is slowly attacked by an aq. soln. of **alum,** and more vigorously when the zinc is in contact with platinum. R. Namias found zinc dissolves completely in neutral soln. of the **persulphates**—according to M. G. Levi and co-workers, with potassium persulphate the action with zinc or cadmium is rapid, with ammonium persulphate it is slower, and, as also shown by J. W. Turrentine, no gas is evolved. According to H. Ditz, a 10 per cent. soln. of ammonium persulphate in sulphuric acid gives off ozonized oxygen.

L. Arons [8] observed that zinc nitride is probably formed in the electric arc between zinc electrodes in **nitrogen,** and appears as a fine deposit on the metal. F. H. Newman also studied the effect of nitrogen on zinc and cadmium as cathodes

in a discharge tube. W. Smith found that when zinc oxidizes in the presence of nitrogen; ammonia, ammonium nitrite and nitrate are formed; and in the spontaneous oxidization of zinc in air, nitrites and nitrates are sometimes produced. W. Smith observed that a hot, nearly boiling soln. of **ammonia** readily acts on zinc cuttings, and still more so on zinc filings; in both cases hydrogen is evolved, and a film of oxide formed which can be readily detached from the metal. W. R. Hodgkinson and N. E. Bellairs also found that zinc dissolves in aq. ammonia while exposed to air, but they did not observe the formation of any nitrite. S. Kappel showed that when the metal is left in contact with air and aq. ammonia, nitrites are formed. According to C. Matignon and G. Desplantes, the oxidation of zinc is not perceptibly augmented by aq. ammonia, the favourable result is a physical effect due to the solvent action of the aq. ammonia on the zinc oxide keeping the surface of the metal clean. G. T. Beilby and G. G. Henderson found that when zinc or brass is heated below its m.p., in a stream of ammonia, there are physical changes in the structure of the metal, and the ammonia is decomposed. A. H. White and L. Kirschbraun obtained a product containing zinc nitride by passing ammonia gas over zinc heated to about 600°. The temp. of decomposition and formation of zinc nitride are so close together that the product is always a mixture of the nitride and the metal. G. G. Henderson and J. C. Galletly showed that cadmium behaves in a similar manner, but a rather smaller proportion is converted into a greenish nitride. W. Weyl found liquid ammonia does not act on zinc, but when sodium-ammonium acts on zinc, sodium diammino-oxide, **zinc diammine,** $Zn(NH_3)_2$, are formed: $2Na(NH_3)+Zn(NH_3)_2O=Zn(NH_3)_2+(NH_2Na)_2O$. He said: silver chloride is sat. with ammonia in one leg of a **W**-tube, an eq. amount of zinc oxide with sodium is placed in the other leg—both legs are then sealed. The silver chloride part is placed in a calcium chloride bath, and the ammonia which is given off is absorbed by the zinc oxide in the other limb. The product is then allowed to act on sodium-ammonium. A deep blue liquid is formed which readily decomposes at 12°–15°. The action of aq. soln. of many **ammonium salts** on zinc is discussed both above and below. T. Curtius and A. Darapsky found that **azoimide** reacts with zinc with the evolution of hydrogen. P. Sabatier and J. B. Senderens found that zinc or cadmium is superficially oxidized by **nitric oxide,** and the metal is oxidized by **nitrogen peroxide** at 300°. The surface of molten zinc becomes matt in an atm. of nitric oxide, and by the action of **nitrous oxide** zinc oxide and nitrogen are formed. F. Emich obtained zinc oxide mixed with a little nitride by passing red-hot nitric oxide over zinc dust. W. R. Hodgkinson and A. H. Coote [9] found that molten **ammonium nitrite** has less action on zinc than it has on cadmium or magnesium, and more than it has on copper, nickel, lead, or bismuth; ammonia is first given off, and the metal nitrate is formed; the nitrate is reduced to nitrite by the hydrogen; the nitrite reacts with the ammonia, and nitrogen is evolved—a gram-atom of cadmium produces a little less than 4 gram-atoms of nitrogen. J. J. Sudborough found **nitrosyl chloride** reacts only slightly with cadmium after many days' exposure at 100°.

When conc. **nitric acid** is poured on melted zinc, the metal becomes incandescent. P. T. Austen said that zinc does not burn in the vapour of nitric acid. N. A. E. Millon found that mono- or di-hydrated nitric acid, free from nitrous acid does not dissolve zinc at —18°, but the metal becomes covered with a yellowish-white film, which prevents further action; as the temp. rises a little above —18°, the film dissolves, and a vigorous action sets in. Zinc retains its metallic lustre in the tetrahydrated acid, and remains unaltered at —18°, but is violently attacked at 0°; a still more dil. acid reacts on zinc even at —18°. H. Braconnot found that conc. nitric acid dissolves zinc less readily than the more dil. acid because of the lower solubility of the product of the reaction in the conc. acid; and an alcoholic soln. of nitric acid acts very slowly with zinc because of the low solubility of zinc nitrate in that menstruum. F. Kuhlmann found that zinc reduces nitric acid forming some ammonia; A. M. Pleischl observed that some nitrous oxide is formed

when nitric acid reacts with zinc, and as the liquid gets hot, an increasing proportion of nitric oxide is formed. H. St. C. Deville showed that the products of the reaction include nitrous acid, nitrous oxide, nitric oxide, ammonia, and a little nitrogen; and, as shown by A. Terreil, E. Divers, and others, free hydrogen never appears as a product of the reaction between zinc and nitric acid. In an attempt to disprove the theory of *l'état naissant*, H. St. C. Deville studied the action of nitric acid of different conc., and of mixtures of nitric acid with sulphuric or hydrochloric acid, and measured the quantities of the acid consumed; he then concluded that each acid pursues its action on the zinc unaffected, except indirectly, by the presence of the other. J. J. Acworth and H. E. Armstrong concluded that in the action of nitric acid on zinc in vacuo, the gaseous product is a mixture of nitrogen and of nitrous and nitric oxides. J. J. Acworth found that in the presence of ammonium nitrate, the gaseous product is mainly nitrogen. A. Bertels stated that when an excess of nitric acid acts on zinc, a basic zinc nitrate is formed.

C. Montemartini made an extensive study of the action of nitric acid on zinc; he showed that the velocity of the dissolution of the zinc in nitric acid increases regularly with the conc. of the acid below 25 per cent.; it then falls slightly, remains constant between 33 per cent. and 42 per cent., then diminishes regularly, attaining its minimum value at a conc. of 68 per cent.; a considerable rise then takes place with increased conc., but the previous maximum value is not again attained. The products formed in the reaction at a low temp. when the acid is in large excess are nitrous acid, hyponitrous acid, nitric oxide, nitric peroxide, nitrous oxide, nitrogen, and ammonia. Under the conditions mentioned, hydroxylamine is not found among the final products of the reaction, and free hydrogen is never evolved. With the exception of nitrous acid and nitric peroxide, the above products are formed, whatever the degree of conc. of the acid; no nitrous acid is, however, formed if the soln. contains more than 30 per cent. of nitric acid, and no nitric peroxide if it contains less. At a temp. of 3°–8°, the quantity of *ammonia* in soln. rises rapidly until the conc. of the acid is 10 per cent., then slowly until a maximum is attained between 40 and 45 per cent.; it falls abruptly at 47 per cent., and at 53 per cent. only a very small quantity is produced, which gradually diminishes with increased conc., and may be represented by a straight line passing through the zero point at 100 per cent. At a temp. of 85°, the maximum occurs at a conc. of 9 per cent., when it is equal to the production at the lower temp.; it then falls rapidly as the conc. is increased to 15 per cent.; beyond this point it may be represented by a line passing through the zero point when the conc. is 100 per cent. At a temp. of 18°–21°, the production of *nitrous acid* increases rapidly with the temp. until a conc. of 14 per cent. of nitric acid is attained; it then falls with equal rapidity with increase of conc. to 30 per cent., at which stage nitrous acid ceases to appear among the final products. Between 18° and 22°, *nitrogen peroxide* is first formed at a conc. of 27 per cent. of acid; it increases slowly at first, rapidly between 64 per cent. and 72 per cent.; beyond 80 per cent. it remains almost constant. The formation of *nitrous oxide* takes place in comparatively large quantities and with great regularity. It reaches a maximum at a conc. of 40 per cent. acid and a minimum at 80 per cent. Nitrogen is formed only in very small quantities in acid of all degrees of conc. Similar results were obtained with cadmium, one gram of which in an excess of 27·5 per cent. nitric acid gave 0·00197 grm. of HN_3; 0·00695 grm. HNO_2; 0·00570 grm. N_2O; 0·00033 grm. N_2; and 0·00216 grm. of NO. J. J. Acworth and H. E. Armstrong obtained more nitric oxide and less nitrous oxide and nitrogen with cadmium than with zinc—*vide* action of nitric acid on magnesium. A mixture of one part of sulphuric acid with 80 parts of water was found by J. M. H. Bigeon to dissolve more zinc than when one part of nitric acid is also present, and J. W. Döbereiner explained the effect by assuming that in the latter case ammonia is formed which neutralizes some of the acid.

E. Divers showed that zinc is very effective in converting nitric acid into *hydroxylamine*, and ammonia is always produced at the same time. He assumes that zinc,

like tin, acts directly upon nitric acid, producing the metal nitrate, and independently, as primary products, ammonia, $4Zn+9HNO_3=4Zn(NO_3)_2+3H_2O+NH_3$; nitrous oxide, $4Zn+10HNO_3=4Zn(NO_3)_2+5H_2O+N_2O$; and nitrogen, $5Zn+12HNO_3=5Zn(NO_3)_2+6H_2O+N_2$. The hydroxylamine also is produced as a primary product when sulphuric or hydrochloric acid is present to form a more stable product: $6Zn+7H_2SO_4+2HNO_3=6ZnSO_4+4H_2O+(NH_2OH)_2.H_2SO_4$. Granulated cadmium acts in a similar manner producing small quantities of hydroxylamine from nitric acid in the presence of sulphuric or hydrochloric acid. V. H. Veley, and H. E. Armstrong believe that nitrous acid is a primary product of the nitric acid whatever be the nature of the reducing agent—hydrogen or metal, or arsenious oxide—and that nitrous acid is invariably formed when any metal is dissolved in nitric acid. E. Divers, on the contrary, regards nitrous acid as a secondary product of the reaction:

> When zinc acts upon nitric acid, neither nitrate nor nitrite or nitrous acid is the primary product, but rather nitrate and hydroxylamine, or ammonia, or nitrous oxide, or nitrogen, or, rather, all these together, but independently and each associated only with the nitrate. If zinc is left in nitric acid, there is undoubtedly a production of nitrite or nitrous acid, which may at last be considerable, but only as a secondary product. Zinc acts freely upon its own nitrate in aq. soln., the products being hydroxide and nitrite. Therefore, only in proportion as nitrate increases in quantity and, before all, nitric acid decreases in quantity, does nitrite or nitrous acid make its appearance.

Although ammonia is produced as a primary product of the reduction, E. Divers showed that it can also be formed as a secondary product as when in the absence of much free acid, hydroxylamine salts, or zinc nitrite, are reduced by zinc to ammonia; nitrous oxide is not only a primary product but it may also arise from the interaction of hydroxylamine with nitrous acid when one of these compounds is formed at a late stage in the reaction and finds the other present, although "they can hardly be supposed to be produced together only to become nitrous oxide and water." Similar remarks apply to nitrogen derived from the interaction of ammonia and nitrous acid. Nitrogen peroxide, and nitric oxide are also assumed to be secondary products derived from the decomposition of nitrous acid respectively by nitric acid and by water. A. von Bijler showed that when $\frac{1}{10}N$-nitric acid acts on zinc at 25°, the ratio of ammonia to the dissolved zinc is as 1 : 35; while the equation: $4Zn+10HNO_3=4Zn(NO_3)_2+NH_4NO_3+3H_2O$, requires a ratio between 1 : 15 and 1 : 16; he attributes the difference to the formation of nitrous acid—no hydroxylamine was observed.

F. Novak found that zinc which has been annealed at 273° dissolves more rapidly in nitric acid than unannealed zinc rolled at 120°. Increasing the amount of lead in the zinc from 0·5 to 2·0 per cent. has very little effect on the speed of dissolution. The cadmium content of zinc conditions the speed of dissolution of the metal. W. W. J. Nicols, A. Krefting, A. Wagner, A. J. C. Snyders, and W. Smith found that soln. of **alkali nitrates** or **alkaline earth nitrates** attack zinc with the evolution of hydrogen. W. R. Hodgkinson and A. H. Coote found that the reaction with cadmium is faster than with zinc; and P. Forstner stated that the formation of alkali nitrite favours the dissolution of the metal. G. Arth found zinc dissolves in **Diver's liquid,** in a sealed tube, forming a crystalline mass. L. Loviton found zinc to be readily soluble in fused **ammonium nitrate** at 160°. W. R. Hodgkinson and A. H. Coote reported that cadmium reacts as fast with an aq. soln. of ammonium nitrate as with the molten salt; and in an ice-cold aq. soln., the metal dissolves without the evolution of any gas—the liquid has an alkaline reaction and gives off nitrogen at 100°. The soln. contains free ammonia and cadmium nitrite. The action of soln. of ammonium nitrate was also studied by A. Bringhenti.

B. Pelletier,[10] and G. Landgrebe melted **phosphorus** with zinc and noticed the two elements combined; and several compounds have since been reported—*vide* phosphides. F. Stromeyer observed a similar behaviour with cadmium and phosphorus. E. Soubeiran,[11] and T. Bergman prepared compounds of zinc and **arsenic**. According to A. Vogel, when a mixture of the two elements is heated, combination sets

in before the mixture gets red hot, and the whole mass glows vividly with a dark red light, and some arsenic volatilizes. According to A. F. Gehlen, a mixture of arsenious oxide with twice its weight of zinc filings, reacts explosively when heated. K. Friedrich and A. Leroux studied a portion of the f.p. curve.

W. Heike obtained the f.p. curves shown in Fig. 17. There are two compounds, Zn_3As_2, melting at 1015°; and $ZnAs_2$, melting at 771°. The former suffers a reversible transformation at 672° into a second modification. Otherwise the curves explain themselves. The alloys have a strong tendency to segregate. A. Descamps prepared some cadmium-arsenic alloys, and S. F. Schemtschuschny obtained the results shown in Fig. 18. The results, so far as they go, resemble

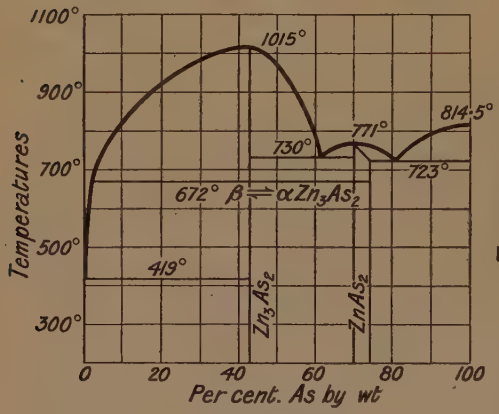

FIG. 17.—Freezing-point Curve of the Binary System: Zn—As.

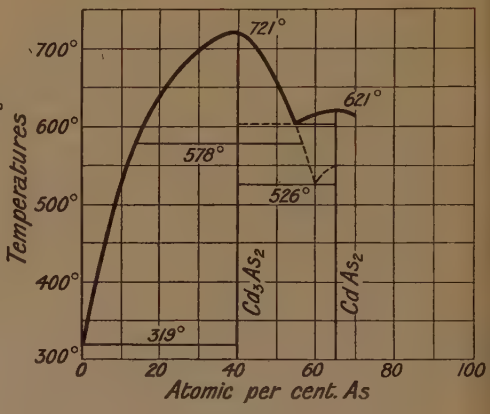

FIG. 18.—Freezing-point Curve of the Binary System: Cd—As.

those with the zinc-arsenic alloys. There are two compounds, Cd_3As_2, melting at 721°; and $CdAs_2$, melting at 621°. W. Spring found that a mixture of powdered arsenic and powdered zinc or cadmium forms an alloy when subjected to great press.

Alloys of antimony with zinc or cadmium are readily formed, and union occurs without the emission of light. The alloys are hard, and brittle, and have a steel-grey colour. The zinc-bismuth alloys were found by C. E. Gellert to have a smaller sp. gr. than the mean of the components. A. F. Gehlen, and A. Vogel also prepared alloys of zinc and antimony; and B. E. Curry, C. R. A. Wright, S. F. Schemtschuschny, H. Gautier and R. Gosselin, and K. Mönkemeyer studied the f.p. curves. The results are summarized in Fig. 19. There are two **zinc antimonides,** Zn_3Sb_2 and ZnSb. The curve shows one maximum, two eutectic points, and two m.p. of the pure metals. The evidence for the existence of the compound Zn_3Sb_2 is as follows. The curve exhibits a distinct maximum corresponding with 45 per cent. of zinc. At 561°, the temp. corresponding with this maximum, the solid which separates is uniform. The crystallization of the fused masses, containing 50 and 40 per cent. of zinc respectively, ends at 411° and 539° respectively. The presence of the compound Zn_3Sb_2 is also deduced from the structure of the alloys, containing from 40 to 50 per cent. of zinc. The evidence for the existence of the compound ZnSb is as follows. The curve exhibits a maximum, corresponding with 35 per cent. of zinc, whilst at 544°, the temp. corresponding with this maximum, the solid which separates is uniform. The crystallization of the fused masses containing 40 and 30 per cent. of zinc respectively ends at 539° and 507° respectively. The structure of the alloys is also evidence for the existence of this compound. J. P. Cooke and E. Elsässer, B. E. Curry, etc., studied the crystalline form of zinc-antimony alloys; J. P. Cooke and E. Maey, the sp. gr.; C. B. Thwing, the thermal expansion; A. Ledebur, the heat of fusion; J. C. Beattie, the behaviour in a

magnetic field; E. Becquerel, W. Rolmann, and A. Seebeck, the thermal e.m.f.; A. Matthiessen, and A. Heil, the electrical resistance; M. Herschkowitsch, and N. A. Puschin, the difference of potential against N-$ZnSO_4$; C. T. Heycock and F. H. Neville, the depression of the f.p.; and A. Stock and W. Doht, and E. Wiederhold, the action of acids. P. Giraud, A. Heil, G. A. le Roy, and K. Mönkemeyer studied the properties of alloys of zinc and antimony along with another element. Alloys of antimony and cadmium have been prepared by B. Wood, P. Christofle, C. R. A. Wright, etc. The f.p. curves have been studied by N. S. Kurnakoff and N. S. Konstantinoff, C. T. Heycock and F. H. Neville, and by W. Treitschke, and the results are summarized in Fig. 20. Two **cadmium antimonides,** Cd_3Sb_2 and

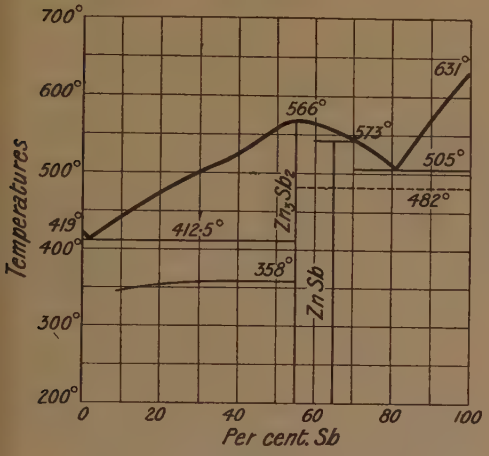

Fig. 19.—Freezing-point Curve of the Binary System: Sb—Zn.

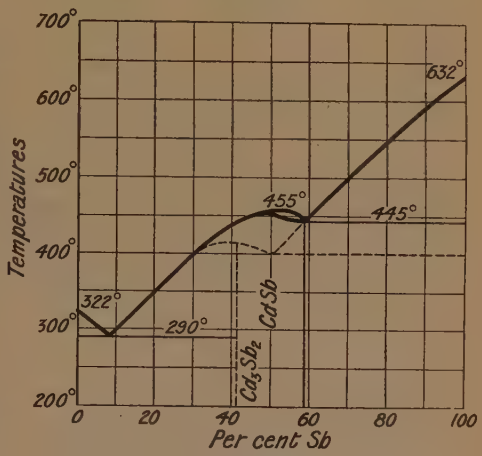

Fig. 20.—Freezing-point Curve of the Binary System: Sb—Cd.

CdSb, appear in the diagram, the f.p. curve for cadmium and antimony takes a different form, according to the conditions of solidification, as, for instance, the nature of the substance covering the metals, the stirring of the mass, the presence of corresponding crystals, etc.; the two latter conditions being necessary for the formation of stable compounds at certain conc. The curve corresponds with four solid phases: (1) antimony, the eutectic point being at 445° and 58·4 per cent. Sb when crystals of the compound CdSb have been added previously, otherwise this part of the curve extends to 402° and composition 52·5 per cent. Sb. (2) The compound CdSb, which separates at 455° from liquid alloys when stirred and cooled quickly. If these alloys are allowed to cool slowly under a layer of carnallite, then the unstable compound Cd_3Sb_2 is formed. (3) The compound Cd_3Sb_2, which commences to separate at 409°. (4) Free cadmium at the eutectic point 296° and 92·5° per cent. cadmium. The alloys containing 42 to 52·5 per cent. antimony, when already solidified, develop heat at 260° to 290°, the temp. rising suddenly by 20° to 30°; this occurs most markedly for alloys containing 50 per cent. antimony, and also for those still richer in antimony if crystals are not added previously and the mass is not stirred while cooling, this sudden rise in temp. being due to the compound Cd_3Sb_2 passing into a more stable form, thus: $Cd_3Sb_2+Sb=3CdSb$. These views are fully confirmed by the microstructure of the various alloys, photographs of which were studied. At conc. 7·5–36 per cent. antimony, the compound Cd_3Sb_2 separates whatever the conditions. E. Maey studied the sp. gr. and the sp. vol. of cadmium-antimony alloys; J. C. Beattie, the behaviour in a magnetic field; C. B. Thwing, E. Becquerel, and A. Battelli, the thermal e.m.f.; W. Iskull, and N. S. Kurnakoff and N. S. Konstantinoff, the crystalline structure.

L. W. Cramer said that zinc does not alloy with **bismuth.** C. M. Marx reported that when equal parts of the two elements are melted together, two layers are

formed. J. Fournet said no chemical compound is formed. The alloys of zinc and bismuth have been studied by F. C. Calvert and R. Johnson, C. R. A. Wright and C. Thompson, etc. The f.p. curve of zinc and bismuth has been studied by C. T. Heycock and F. H. Neville, H. Gautier and R. Gosselin, B. E. Curry, W. Spring and L. Romanoff, and by P. T. Arnemann. The results are illustrated in Fig. 21. The alloy separates into two layers, a soln. of bismuth in zinc and of zinc in bismuth. The course of the two solubility curves is shown by the dotted curve in Fig. 21. It was studied by C. R. A. Wright, B. E. Curry, H. Gautier and R. Gosselin, F. Guthrie, and W. Spring and L. Romanoff. The latter found :

	266°	419°	475°	584°	650°	750°	
Upper layer (Zn in Bi) .	—	97·0	95·0	90·0	85·0	73·0	per cent.
Lower layer (Bi in Zn) .	86·0	—	84·0	80·0	77·0	70·0	„

and the two elements are completely miscible at 850°. The sp. gr. and sp. vol. of zinc-bismuth alloys was studied by E. Maey, and H. Gautier ; the heat of fusion by G. G. Person ; the lowering of the f.p. by C. T. Heycock and F. H. Neville ; the thermal e.m.f. by E. Becquerel, W. Rolmann, and A. Seebeck ; the potential against N-$ZnSO_4$ soln. by M. Herschkowitsch, and A. Sucheni, and against a soln. of sodium chloride by A. P. Laurie and H. le Chatelier ; and the action of nitric acid by C. Montemartini and E. Colonna. G. W. A. Kahlbaum and E. Sturm obtained an alloy by the compression of the mixed powders. The f.p. curve of the alloys of cadmium and bismuth has been studied by A. W. Kapp, and by A. Stoffel, with the results shown in Fig. 21. This is a typical V-eutectic curve. The alloys

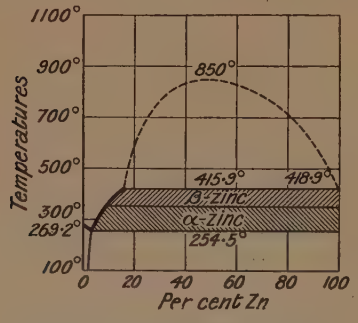

Fig. 21.—Freezing-point Curve of the Binary System : Bi—Zn.

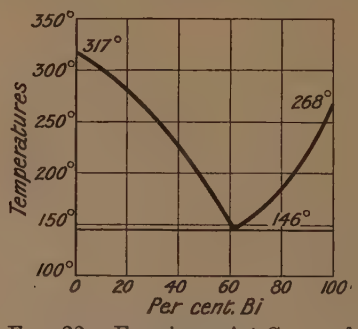

Fig. 22.—Freezing-point Curve of the Binary System : Bi—Cd.

have been studied by C. R. A. Wright, H. Behrens, and F. Guthrie. A. Matthiessen, G. Vicentini and D. Omodei, F. Rudberg, and E. Maey investigated the sp. gr. and sp. vol. of the cadmium-bismuth alloys ; C. T. Heycock and F. H. Neville, and P. Siloff, the lowering of the f.p. ; the thermal e.m.f. by C. C. Hutchins, A. Battelli, and D. Mazzotto ; and M. Herschkowitsch, the difference of potential against N-$CdSO_4$ soln. E. Becquerel, and J. C. Beattie studied the ternary alloys Cd—Bi—Sb ; and C. R. A. Wright, and W. D. Bancroft, Cd—Bi—Zn.

B. Reinitzer and H. Goldschmidt [12] found that zinc reacts with **phosphoryl chloride** at ordinary temp. and more rapidly at 100°, forming zinc chloride, zinc metaphosphate, and a red substance—red phosphorus or phosphorus suboxide. Zinc reacts with **phosphoric acid,** forming the phosphate and phosphide. A. Bringhenti, A. Krefting, and A. J. C. Snyders studied the action of soln. of the **alkali phosphates.** W. Smith found that with a boiling soln. of **ammonium phosphate,** zinc gives hydrogen and ammonia ; and with a boiling soln. of **ammonium arsenate,** it gives hydrogen and arsine. A. Krefting studied the action of soln. of **sodium arsenate, sodium tungstate,** and **potassium antimonate.** W. Thomson found that the electrolytic reduction of soln. of **arsenites** or **arsenates** proceeds more rapidly with a zinc than with a lead cathode.

As previously indicated nearly all commercial zinc contains some **carbon,** which J. J. Berzelius,[13] F. A. C. Gren, and R. Schindler assumed to be present as *zinc carbide;* the black powder which remains after the distillation of zinc cyanide, and which when ignited burns, forming zinc oxide, was also supposed by J. J. Berzelius to be zinc carbide. There is, however, no evidence of the formation of a carbide under these conditions. O. Ruff and B. Bergdahl found that cadmium and zinc dissolve only traces of carbon. M. Berthelot heated zinc with **carbon monoxide** in a sealed tube at 550° for many hours, and obtained a trace of carbon dioxide and carbon; **carbon dioxide** acts as an oxidizing agent on zinc vapour—*vide* the preparation of zinc. According to F. Wöhler, a soln. of **sodium carbonate** forms a soluble basic carbonate, $NaO.Zn.NaCO_3$, and hydrogen is evolved. W. Smith found a boiling soln. of sodium carbonate was decomposed by zinc, forming hydrogen and zinc oxide; but, unlike F. Wöhler, he could find no zinc in the soln.; nor did H. W. F. Wackenroder find any attack on zinc oxide by a boiling soln. of sodium carbonate. A. Bringhenti studied the action of soln. of **ammonium carbonate,** and of **ammonium oxalate.** G. A. Goyder found that zinc dissolves in an aq. soln. of **potassium cyanide** with the evolution of a gas; the reaction has been studied by F. Kunschert, F. Spitzer, and H. A. White. A. Brochet and J. Petit found that under the influence of the alternating current, the attack by potassium cyanide results in the evolution of hydrogen, but it is arrested on account of the formation of a sparingly soluble complex salt $ZnCy_2.2KCy$; with cadmium, the attack is continued by the aid of atm. oxygen and is concentrated on the portion of the strip near the surface of the liquid. A. Krefting studied the action of soln. of **potassium ferrocyanide,** and of **potassium ferricyanide.** Differences of electric potential of different parts of a piece of zinc or cadmium are shown by dipping the metal in an agar-gel containing potassium ferrocyanide and phenolphthalein. A. Bringhenti studied the action of soln. of **ammonium thiocyanate** and of **potassium thiocyanate.** According to G. Chesneau, dil. **acetic acid** attacks zinc more than does a *N*-soln. of **sodium acetate.** S. H. Mathews found that a soln. of **trichloro-acetic acid** in nitrobenzene acts vigorously on zinc. Zinc is attacked by **carbon tetrachloride** in the presence of moisture, but **dichloroethylene, trichloroethylene,** and **perchloroethylene** are virtually inactive.[14] N. N. Beketoff found **silicon tetrachloride** vapour is reduced to silicon and **boron trifluoride** is reduced to boron.

Zinc dissolves slowly in **alcohol,** and, according to T. Roman and G. Delluc,[15] 0·006 grm. of zinc is dissolved per litre. M. Traube showed that absolute alcohol is not oxidized in air by zinc, but when diluted with water oxidation occurs, and this the more, the greater the proportion of water present. W. Ipatjeff, and H. Jahn have studied the action of zinc as a catalytic agent in the oxidation of alcohol to aldehyde, and the former found this metal is more active than copper, nickel, cobalt, iron, manganese, or chromium. Acetaldehyde is converted by zinc at an elevated temp. into carbon monoxide and methane. The effect of zinc on alcoholic liquids—wine, beer, and spirits—has been investigated by R. P. Duchemin, F. Malméjac, G. Heinzelmann, L. A. Levat, L. Nathan and A. Schmidt, and C. Sellenscheidt. The **fatty acids** were found by J. Pässler [16] to attack zinc slowly. A. Mailhe studied the oxidation products. Z. Crommydis found that in the presence of zinc **oxalic acid** is reduced to glycollic acid. J. J. Redwood, and C. Engler and E. Kneis, found that zinc is not affected by **mineral lubricating oil;** the former also found that zinc is very little affected by **rape oil, olive oil,** or **tallow oil;** it is attacked most by **sperm oil,** less by **cotton-seed oil,** and less still by **lard oil;** but W. van Rijn found that zinc is attacked by olive oil and **castor oil,** and that **sesame oil** in a zinc vessel formed zinc palmitate, oleate, and stearate. A. Gawalowsky found zinc is but little attacked by rape oil. S. Fokin found zinc acts catalytically on the oxidation of **linseed oil.** D. Klein and A. Berg found a soln. of **sugar** at 115°–120° attacks zinc with the evolution of hydrogen, and the development of an acid; and F. Plzak and B. Husek found that the presence of zinc in palladium

makes the alloy retard the inversion of cane-sugar. Zinc was found by C. O. Weber to have very little action on sulphuretted caoutchouc.

A. Pospieloff[17] found the vapour of zinc attacked the **platinum** electrodes in a discharge tube, but not **iron** or **aluminium** electrodes. In his study on **metallic precipitation,** N. W. Fischer noted that zinc or cadmium precipitates the metals from most of the ordinary salts of copper, silver, gold, cadmium (by zinc only), mercury, tin, lead, tellurium, bismuth, arsenic, antimony, iron, platinum, palladium, rhodium, iridium, and osmium, but not nickel—*vide* the individual metals, and the observations of J. A. Poumarêde, L. de Boisbaudran, A. Destrem, and A. Villiers and F. Borg. In some cases, the metallic precipitation is utilized in quantitative analysis. E. Witting, J. B. van Mons, and J. B. Senderens found that zinc reduces lead from a soln. of lead acetate. T. E. Thorpe found that the reducing action of a definite amount of zinc on ferric salts increases with increased conc. and decreasing acidity of the soln. H. Munk found that zinc which has been in contact with a dil. soln. of alkali carbonate for a long time becomes more electronegative and precipitates copper from soln. less rapidly than ordinary zinc. Copper is precipitated from a soln. of copper oleate in cresol at 100°, and the addition of water favours the reaction; manganese, chromium, nickel, cobalt, iron, and cadmium were found by J. L. Sammis to be ineffective. For the action of soln. of **chromic acid** and **chromates** *vide* passive zinc. As W. R. Grove and others have shown, zinc may be regarded as an energetic **reducing agent**—particularly when in a powdered form—*e.g.* it reduces the chromates and permanganates; and with it C. Stahlschmidt reduced nitrates to nitrites; M. Delépine reduced tungstic oxide to tungsten; L. Troost reduced sodium zirconium chloride; and M. Dullo reduced sodium aluminium chloride. Powdered zinc has been much used as a reducing agent in organic chemistry. In the theory of the nascent state, the formation of hydrogen precedes the reduction, so that the reduction is due to a secondary reaction following the main reaction. J. Swinburne claimed that when zinc reacts with acid so as to reduce a ferric salt, it is better to say that when the metal dissolves it can either reduce a ferric salt or generate hydrogen. Of the two reactions, the reduction of the ferric salts consumes the less energy and so takes place. If no reducible salt be available, hydrogen gas is evolved, and much work is needed for its expansion, against atm. press., into the gaseous form.

If a piece of metallic zinc be immersed in a one per cent. soln. of copper sulphate, copper is precipitated on the zinc. When the zinc has been coated with a layer of copper, it can be removed from the soln., washed with water, and dried. The mixture of copper and zinc is called a **copper-zinc couple.**[18] The couple can also be made by heating a mixture of nine parts of powdered zinc with one part of powdered copper in a flask until the zinc begins to flow. Let the mixture cool in a closed flask. The zinc is now much more active chemically, for, unlike metallic zinc alone, it can decompose water at ordinary temp. The zinc and copper act electrolytically. Metals which are chemically combined or alloyed together do not act in the same way. The two metals, one deposited upon the other, form a galvanic couple. The zinc-copper couple also reduces hydroxylamine hydrochloride to ammonium chloride, nitrates and nitrites to ammonia; chlorates to chlorides; arsenates to arsine, etc. The couple is also an important reducing agent in organic chemistry.

The metallic precipitation of zinc and cadmium.—S. Kern,[19] and F. Faktor stated that metallic zinc is precipitated from soln. of its salts by *magnesium*, and with a conc. soln. of zinc chloride much hydrogen is evolved. With a hot or cold, conc. or dil. soln. of zinc sulphate, E. G. Bryant obtained about a 50 per cent. yield of metallic zinc. H. N. Warren made a *zinc-tree*, by wrapping a magnesium rod in asbestos paper, and immersing the roll in a soln. of zinc chloride. W. Eidmann found that the decomposition of zinc cyanide by magnesium is vigorous, and is accompanied by incandescence, forming magnesium nitride, zinc, and carbon. G. McP. Smith found a conc. soln. of zinc cyanide gives a precipitate of zinc when

treated with *copper*. According to K. Seubert and A. Schmidt, G. Post, and A. J. C. Snyders, when a neutral aq. soln. of zinc chloride is treated with *zinc* filings, zinc hydroxide and a basic chloride are formed; while an ammoniacal soln. gives a precipitate of zinc and zinc hydroxide, but about 20 per cent. of zinc remains in soln.; the precipitation is also incomplete with hydrochloric acid soln. M. Centnerszwer and J. Drukker measured the rate of precipitation of copper from soln. of cupric sulphate by zinc. They found evidence of a period of induction, and that if C denotes the conc. of the copper in soln., and C', the conc. of the copper at the surface of the metal, while x denotes the amount of copper precipitated by a zinc plate of surface S, then $dx/dt=kS(C-C')$. If the reaction at the surface of the zinc is instantaneous, $C'=0$. If C_0 denotes the initial conc. of the soln., and v its vol., $x=(C_0-C)v$, and $dx/dt=-v.dC/dt$. Hence, $-vdC/dt=kSC$, or $k=2{\cdot}303v(\log C_0-\log C)/St$. J. L. Davis also studied the precipitation of metals by zinc.

F. Faktor [20] found that cadmium hydroxide is precipitated when a soln. of a cadmium salt is treated with *magnesium*—hydrogen is at the same time evolved. C. Formenti and M. G. Levi found that *aluminium* energetically reduces an aq. soln. or a molten cadmium salt; C. Goldschmidt found that cadmium is quantitatively precipitated by boiling in a vessel of aluminium an aq. soln. of a cadmium salt, mixed with a little cobalt or chromium nitrate. G. McP. Smith observed that *copper* precipitates cadmium from a conc. aq. soln. of cadmium sulphate in potassium cyanide. P. N. Raikow and O. G. Georgiew found that powdered *iron* forms a ferrous salt when treated with a neutral soln. of cadmium nitrate, sulphate, chloride, bromide, or iodide, but not the chlorate. J. L. Sammis found that *lead* is covered with a black film when boiled for 2 hrs. with a soln. of cadmium oleate in toluene, while magnesium, aluminium, antimony, bismuth, zinc, cadmium, tin, iron, nickel, cobalt, copper, or silver does not act in this way.

The electrodeposition of zinc and cadmium.—The electrodeposition of zinc from *neutral solutions* has been investigated by A. Minet,[21] C. J. Zimmermann, F. F. Exner, etc.; of cadmium from neutral soln. by A. Hollard,[22] H. Senn, E. F. Smith, A. Classen, A. Fischer, etc.; of zinc from *acid solutions* by T. S. Price,[23] W. D. Bancroft, S. Cowper-Coles, etc.; of cadmium from acid soln. by C. Luckow,[24] A. Classen, S. Avery and B. Dales, M. Heidenreich, E. F. Smith, etc.; of zinc from *cyanide solutions* by C. Luckow,[25] F. Beilstein and L. Jawein, M. le Blanc and K. Schick, etc. C. J. Werlund recommended the following cyanide bath for zinc plating, the values being oz. per gallon: $Zn(CN)_2$, 8; NaCN, 7; NaOH, 1 or 2; Na_2CO_3, 4; NaF, 1; corn syrup, 1; gum arabic, $\frac{1}{8}$; temp. of bath, 40°–50°; voltage, 3–5. Very smooth, greyish-white deposits were obtained. The electrolyte does not deteriorate on standing, and can be used with a high current density even in mechanical plating units where the cleaning is poor. The electrodeposition of cadmium from cyanide soln. has been investigated by A. Brunner,[26] A. Fischer, W. Stortenbecker, etc.; of zinc from *solutions of alkali zincates* by F. Weil,[27] C. Beslay, W. D. Bancroft, F. Förster and O. Günther, etc.; of cadmium from alkali soln. by W. S. Lorimer and E. F. Smith,[28] E. F. Smith and F. Muhr, T. Moore, etc.; and of zinc from *ammoniacal solutions* by F. Förster and co-workers,[29] T. S. Price, L. H. Ingham, etc. The effect of various additions to the electrolyte have been tried; for instance, F. Förster and O. Günther [30] tried a soln. of zinc chloride sat. with zinc oxychloride; J. Rontschewsky, chloric acid; H. Paweck, boric acid or borates, C. F. Burgess, C. C. Person, L. Potthoff, A. van Winkle, E. Kaselowsky, and G. Langbein, aluminium salts; A. Schaag and co-workers, J. Szirmay and L. von Kollerich, and R. de Montgelas, magnesium salts; C. F. Burgess, A. Schaag and R. Falk, G. Langbein, O. Gabran, and O. Lehmann, tin salts; H. Leitner, manganese salts; S. Cowper-Coles, iron salts; and J. Burrow, A. Schaag and R. Falk, mercuric salts. W. D. Bancroft found the presence of cadmium, iron, lead, and copper produces bad results because these metals may be deposited before the zinc. The addition of several organic

compounds or salts of organic acids has been tried: A. van Winkle, gelatine; J. Szirmay and L. von Kollerich, dextrose; W. D. Bancroft, glue; J. Meurant, gum; A. Classen, and S. A. Tucker and E. G. Thomssen, glucosides; G. Langbein, dextrose; A. Brester, L. Trunkhain, sugar (maltose and dextrose) and yeast; L. Potthoff, A. Schaag and co-workers, acetic, citric, or tartaric acid; E. C. Broadwell, phenol, aldehyde, carboxylic acids; E. D. Kendall, glycerol; W. D. Bancroft, formaldehyde; G. Langbein, urea; and E. Goldberg, amines, amides, cyanides, nitriles, and pyridine and quinoline bases. A. Mazzucchelli found, with a low current density, small additions of salts of quinine, cinchonine, quinoline, dimethylaniline, α-naphthylamine, lutidine, aniline, pyridine, and gelatin, using a zinc anode, and a brass cathode, homogeneous, uniform, and fine-grained deposits of zinc can be obtained. Q. Marino electrolyzed soln. of zinc salts in glycerol; and H. E. Patten, soln. of zinc salts in acetone. G. Carrara electrolyzed methyl alcohol soln. of cadmium salts.

The electrolysis of molten zinc chloride and iodide was studied by M. Faraday in 1833; and the work has been extended by R. Lorenz [31]—with and without additions of ammonium, potassium, sodium, or magnesium chloride. The effect of other chlorides—lead, iron, copper, and silver—has been tried. J. Swinburne,[32] R. Lorenz and co-workers, O. H. Weber, A. Helfinstein, H. Frei, etc., electrolyzed fused cadmium chloride. V. Czepinsky has studied the electrolysis of zinc bromide; and O. H. Weber, of cadmium bromide. The *alternating current electrolysis* of zinc salts has been investigated by B. Rösing,[33] M. le Blanc and K. Schick, A. Löb, etc.; and of cadmium salts by J. W. Richards,[34] M. le Blanc and K. Schick, A. Löb, A. Brochet and J. Petit, H. Danneel, etc. The choice of *anodes* has been studied by J. W. Langley,[35] G. Langbein, A. G. Betts, etc., and the choice of *cathodes* by A. Gockel,[36] H. Nissenson, H. Paweck, etc.

Reactions of zinc and cadmium of analytical interest.—Neither zinc nor cadmium salts give a precipitate with hydrochloric acid, and zinc does not give a precipitate with **hydrogen sulphide** in acid soln., although cadmium salts give a yellow precipitate of cadmium sulphide, which, unlike the yellow precipitate of arsenic sulphide, is insoluble in alkali sulphides, soluble in a large excess of hydrochloric acid, in warm dil. nitric acid, or boiling dil. of sulphuric acid (1 : 5). According to F. Jackson,[37] one part of cadmium in 16,000 parts of soln. can be detected by hydrogen sulphide. A neutral soln. of a zinc salt precipitates zinc sulphide incompletely when treated with hydrogen sulphide, $ZnCl_2+H_2S \rightleftharpoons 2HCl+ZnS$; the precipitate is soluble in mineral acids, so that the reaction is reversible. Zinc sulphide is insoluble in acetic acid, so that if the soln. of zinc salt contains sodium acetate, the zinc may be quantitatively precipitated by hydrogen sulphide: $ZnCl_2+2NaC_2H_3O_2+H_2S=2NaCl+2HC_2H_3O_2+ZnS$. Similar remarks apply to weaker acids other than acetic.

Neutral or alkaline soln. of zinc salts give a colloidal precipitate of zinc sulphide when treated with **ammonium sulphide**: $ZnCl_2+(NH_4)_2S=ZnS+2NH_4Cl$. The precipitate is more granular and more easily filtered and washed if it be obtained with boiling soln. in the presence of a considerable proportion of ammonium salts, so that hydrogen sulphide or an alkali sulphide gives a precipitate in an ammoniacal soln. of a zinc salt. According to J. L. Lassaigne, one part of zinc sulphate in 10,000 parts of water gives flakes of the sulphide with potassium sulphide, and with 20,000 parts of water, a faint opalescence. F. Jackson said that one part of zinc in 8000 parts of soln. can be detected by means of ammonium sulphide. According to B. Neumann, and E. Mylius, the ferrocyanide reaction for zinc is more sensitive than that with ammonium hydroxide, carbonate, or hydrosulphide, especially working with hot soln. and avoiding an excess of the precipitant. E. Jordis gave the sensitiveness as 1 in 3,000,000. Cadmium salts under similar conditions give a yellow colloidal cadmium sulphide which is coagulated if it be formed in a conc. salt soln. When zinc salts are treated with **alkali** a white gelatinous hydroxide is precipitated which is soluble in excess, forming a soln. of alkali zincate, say, $Zn(OK)_2$; when a dil. aq.

soln. of the alkali zincate is boiled, hydrolysis occurs, and zinc hydroxide is precipitated. The corresponding hydroxide precipitated from cadmium salts by alkali hydroxides, is not soluble in an excess, and when gently ignited, furnishes a brown-coloured oxide. F. Jackson found that one part of zinc or cadmium in 4000 parts of soln. can be detected by sodium hydroxide. Aq. **ammonia** precipitates white zinc hydroxide from neutral soln. The precipitate is soluble in ammonium salts because of the formation of a soluble complex salt; zinc hydroxide is also soluble in an excess of ammonia because of the formation of a soluble complex salt, $[Zn(NH_3)_6](OH)_2$; and in the presence of ammonium salts, say, ammonium chloride, the soluble complex $[Zn(NH_3)_6]Cl_2$ is formed. Similar results are obtained with nickel, manganese, magnesium, or iron salts. Ammonia also precipitates white cadmium hydroxide which, unlike lead hydroxide, is soluble in an excess owing to the formation of a soluble complex hexammino-salt as in the case of zinc. When the soln. of the complex is diluted and boiled, cadmium hydroxide is re-precipitated. According to F. Jackson, soln. containing one part of zinc in 8000 and one part of cadmium in 4000, give precipitates with aq. ammonia; T. G. Wormley said one part of zinc in 12,500 can be detected by aq. ammonia.

A white basic carbonate, like the corresponding magnesium compound, is precipitated on adding an **alkali carbonate** to a soln. of a zinc or cadmium salt. The precipitate is not soluble in excess. According to J. L. Lassaigne, a soln. of one part of zinc sulphate in 10,000 parts of water gives flakes of the precipitate with sodium or potassium carbonate, but with 20,000 parts of water the precipitate appears only after some time. T. G. Wormley detected one part of zinc in 12,500 parts of soln. by means of sodium carbonate, and F. Jackson one part of zinc in 8000 parts of soln., and one part of cadmium in 4000 parts of soln. A soln. of **ammonium carbonate** behaves in a similar manner; except that the precipitate with the zinc salt is soluble in excess, but insoluble with the cadmium salt, the precipitation does not occur in the presence of ammonium chloride. According to J. N. von Fuchs, zinc salts are not precipitated by calcium carbonate, but, according to H. Demarçay, although zinc salts give no precipitate with **barium carbonate,** if the mixture is boiled, all the zinc is precipitated as basic carbonate. Similar remarks apply to the carbonates of strontium, calcium, and magnesium. Zinc sulphate of course decomposes barium carbonate. Cadmium salts are not changed.

When a soln. of a zinc salt is treated with **potassium cyanide,** a white precipitate of zinc cyanide is formed: $ZnCl_2+2KCy=2KCl+ZnCy_2$, which is soluble in excess owing to the formation of a soluble complex, K_2ZnCy_4. This complex is decomposed by acids: $K_2ZnCy_4+2HCl=2KCl+2HCy+ZnCy_2$; and by alkali sulphides: $K_2ZnCy_4+(NH_4)_2S=2KCy+2NH_4Cy+ZnS$. Cadmium salts also give white cadmium cyanide under similar conditions, and this too is soluble in excess owing to the formation of a soluble complex, K_2CdCy_4. Alkali hydroxides and carbonates do not give a precipitate with a soln. of potassium cadmium cyanide, but hydrogen sulphide precipitates yellow cadmium sulphide. F. Jackson detected one part of cadmium in 1000 parts of soln. by means of potassium cyanide. When zinc salt soln. are treated with **potassium ferrocyanide,** they furnish a white precipitate of zinc ferrocyanide, Zn_2FeCy_6, which is changed by an excess of the potassium salt into insoluble potassium zinc ferrocyanide, $Zn_3K_2(FeCy_6)_2$. According to J. L. Lassaigne, one part of zinc sulphate in 10,000 parts of water gives a slight turbidity with potassium ferrocyanide; with 20,000 parts of water a very slight turbidity; and with 80,000 parts of water, the turbidity does not appear until after 5 to 10 mins. When **potassium ferricyanide** is added to a soln. of a zinc salt, a brownish-yellow precipitate of zinc ferricyanide is formed which is soluble in ammonia and in moderately conc. hydrochloric acid. No precipitate is formed when a soln. of a cadmium salt is treated with **potassium thiocyanate** alone or after the addition of sulphurous acid. **Ammonium thioacetate** gives no precipitate with zinc salts in acid soln., but zinc sulphide is precipitated from ammoniacal soln. When zinc salts are treated with **sodium phosphate** they furnish a gelatinous precipitate

of normal zinc phosphate: $4Na_2HPO_4+3ZnCl_2=2NaH_2PO_4+Zn_3(PO_4)_2+6NaCl$; the precipitate soon becomes crystalline and then filters readily; it is soluble in ammonia and in acids. Cold soln. of cadmium salts gives no precipitate with **potassium chromate,** but a boiling soln. gives a precipitate of yellow basic chromate, $Cd_2(OH)_2CrO_4$. F. Jackson said that one part of cadmium in 1000 parts of soln. can be detected by the precipitate produced with potassium dichromate. Cadmium salts give no precipitate with chromic acid. Cadmium and zinc salt soln. give no precipitate with **sodium thiosulphate,** or with **sodium sulphite**. S. R. Benedict obtained a white precipitate when **potassium periodate** is added to a soln. of a zinc salt. The presence of ammonia hinders the precipitation. A 17 per cent. soln. of **potassium perchlorate** was found by R. Salvadori to give a white crystalline precipitate with ammoniacal soln. of cadmium salts. A. del Campo Cerdan reported that when an alcoholic or ethereal soln. of **resorcin** is added to ammoniacal soln. of resorcin a blue coloration is produced. The reaction is characteristic if salts of cadmium, copper, cobalt, nickel, or manganese be absent. A soln. of **potassium oxalate** produces a white crystalline precipitate with a soln. of a zinc salt; the resulting zinc oxalate forms a soluble double salt with an excess of the precipitant; and the double salt is decomposed by acetic acid reprecipitating zinc oxalate. Alkali sulphates, acetates, formates, and succinates do not give precipitates with zinc salts, but a mixed precipitate is formed if some chromium salt is present as well.

The uses of zinc and cadmium.—Galvanizing is perhaps the most important use to which metallic zinc is put. In 1837, H. W. Cranfurd [38] coated well-cleaned surfaces of iron by simple immersion in a bath of molten zinc. The operation is called **galvanizing,** and the coated metal **galvanized iron.** Previously, iron was coated by galvanic agency, hence the name. Although the galvanic process was practically ousted by H. W. Cranfurd's process, the electrolytic process is a serious competitor, even though the surface is dull and dead and not so bright as in the hot immersion process. The advantages of the galvanic process turn on (i) greater economy in the use of the metal; (ii) better control of the thickness of the coating; and (iii) its use for special articles of steel, etc., whose temper would be injured by immersion in a bath of molten zinc.

In **dry galvanizing,** or **sheradizing** the cleaned articles of iron or steel are heated in metal boxes or drums alone with zinc dust at a temp. between 260° and 425°. The zinc is partially volatilized, and the vapour condenses on the surface of the metal to be plated.[39] The sheradized surface is light grey and matt, but it can be polished to rival nickel plate. The process was devised by S. Cowper-Coles about 1902; it is adapted for coating articles with a pattern or design on the surface which would be filled up or obliterated by ordinary hot galvanizing. Metals, etc., can also be coated with a protective or ornamental film of some other metal by **spraying.** In Scoop's process [40] the spray is driven at a high velocity against the body to be coated.

Spelter is used for making ornamental slush or hollow castings where the metal is poured from the mould as soon as the surface has solidified. Rolled zinc plates are used for domestic articles; as an anti-corrosive agent in steam boilers where the zinc plates bolted to the boiler are attacked first and renewed as required. Cast zinc rods are used for batteries; seamless zinc pipes for cold-water supplies may be tin-lined. Zinc is cheaper than lead for this purpose, but the expansion is too great if hot water is to be transported. Zinc is used in the manufacture of a large number of alloys—*vide* brass. The addition of zinc to certain alloys gives them increased wearing powers, and it is therefore added to bearing metals, bronze coinage, etc.; and as a precipitant for gold in the cyanide process; it is also used in Parkes' process for desilvering lead; and in zincography. Zinc dust is employed as a reducing agent in the dyeing industry. Many of the compounds of zinc, such as the oxide, chloride, sulphate, and carbonate, are employed for a great variety of medicinal and industrial purposes. P. Drinker has reviewed the bibliography on the **toxicity of zinc** —*vide* zinc oxide. C. O. Johns and co-workers, and E. W. Schwartze and

C. L. Alsberg have also studied the physiological action of zinc and cadmium salts. J. Czochralsky and E. Lohrke have discussed the *zinc pyrophoric alloys*.

Cadmium is used in making low temp. melting alloys—tips of automatic sprinklers, safety plugs for boilers, electric fuses, stereotype plates, and solders. Cadmium is stated by C. E. Siebenthal and A. Stoll [41] to be a better rust preventer than nickel, so that it has a greater tendency than nickel to tarnish. When alloyed with a little silver, it is used for plating the bright parts of bicycles, etc. An alloy of cadmium with 7·5 per cent. of silver withstands the influence of the atm. better than silver with an eq. amount of copper. A fraction of one per cent. of cadmium is used as a deoxidizer in making bronze telegraph and telephone wires and cables in France and Italy. It is also used as a deoxidizer in making nickel alloys. A cadmium band on the hard-jacketed cartridge ball of small arms ammunition, is said to take the rifling with little wear on the barrel, and thus prolongs the life of the gun. Cadmium amalgam was formerly used by dentists for stopping teeth. Cadmium sulphide is used for making yellow pigments, although it is too costly for general consumption.

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§ 7. The Atomic and Molecular Weights of Zinc and Cadmium

J. J. Berzelius estimated that the at. wt. of zinc is about four times the hydrogen eq., 33, and zinc oxide, now symbolized ZnO, was symbolized ZnO_2. A number approximating to 65·4 for the at. wt. of zinc is in agreement with Dulong and Petit's sp. ht. rule; with Mitscherlich's isomorphic rule; with the periodic rule; and with the vap. density of the volatile compounds of zinc—*e.g.* according to V. and C. Meyer,[1] the vap. density of zinc chloride is of the order 131·2 to 133·5, which is in agreement with the at. wt. 65·4 as the smallest value for the at. wt. of zinc. A similar conclusion follows from the vap. density of zinc ethyl, and other volatile zinc compounds; and from the determinations of the mol. wt. of zinc salts in soln. Similar remarks apply also to cadmium for the different properties of this element,

and the vap. density of cadmium iodide, measured by A. Scott, corresponds approximately with the at. wt. 112.

According to O. Meyer and co-workers, the **vapour density** of zinc is between 2·36 and 2·41, when the calculated value for a monatomic mol. is 2·25 ; H. Biltz obtained 2·64 between 1732° and 1748°. H. von Wartenburg also measured the vap. density in argon between 1200° and 2070°, and obtained a mean value corresponding with a mol. wt. of 70·4. The monatomic nature of the zinc molecule is confirmed by A. F. Krafft and P. Lehmann's determination of the b.p. of zinc in vacuo in the cathode rays. J. Traube also inferred that molten zinc has monatomic mols. in promixity to the b.p. This is also confirmed by W. Vaubel, and G. G. Longinescu. P. Walden also came to the same conclusion from his work on the surface tension. From the f.p. of soln. of zinc in mercury G. Tammann assumed that the zinc in soln. has monatomic mols. G. Meyer, and G. McP. Smith came to a similar conclusion. C. T. Heycock and F. H. Neville also measured the depression of the f.p. of zinc in molten cadmium, lead, or bismuth. According to W. Broniewsky, at the lower temp. the zinc mol. probably becomes more complex because, like iron, cobalt, and nickel, its dilation and electrical resistance change up to a definite critical temp. at which the mols. become monatomic—similar discontinuities are obtained with the thermal e.m.f. and the sp. ht. P. Walden obtained 1·5 for the association factor ; J. Traube, 1·0 ; W. Vaubel, 4·4 ; and G. G. Longinescu, 5·0.

H. St. C. Deville and L. Troost [2] found the vap. density of cadmium to be 3·94 ; H. Biltz, 4·34 to 4·38 ; the calculated value for a monatomic vapour is 3·87. G. Meyer, and H. Biltz and V. Meyer also obtained results in agreement with this assumption. A. F. Krafft and P. Lehmann assumed that the cadmium mol. is monatomic, from observations on the b.p. of the metal in vacuo when exposed to cathode rays. G. Meyer calculated the mol. wt. of cadmium from the difference in potential of two amalgams of different conc. in a soln. of potassium iodide, but F. Haber showed that it is not possible to distinguish by electrometry the difference in effects produced from monatomic mols. and the formation of complexes. W. Ramsay and G. McP. Smith obtained results in agreement with the assumption that the metal forms monatomic mols. when dissolved in mercury. G. Tammann drew a similar conclusion from the f.p. of soln. in mercury, and C. T. Heycock and F. H. Neville from soln. in bismuth or tin. From observations on the surface tension of fused cadmium, P. Walden concluded that the mols. of fused cadmium are probably monatomic. W. Broniewsky concluded that the cadmium mol. shows no association at —183°. P. Walden and J. Traube obtained 1·0 for the association factor ; G. G. Longinescu, 3·0 ; and H. Siedentopf, 1·7.

J. L. Gay Lussac [3] made the first determination of the at. wt. of zinc by oxidizing the metal in nitric acid and measuring the evolved hydrogen, but J. J. Berzelius, in 1811, dissolved zinc in nitric acid, evaporated the soln. to dryness, and calcined the residue. The results correspond with the at. wt. 64·51.

V. A. Jacquelain, in 1842, determined the ratio Zn : ZnO by converting the metal into nitrate, and igniting the nitrate for the oxide as done by J. J. Berzelius ; he calculated from the Zn : ZnO, 66·23. A. Erdmann employed a similar process, and obtained 65·05 ; H. N. Morse and W. M. Burton likewise obtained 65·46 ; and H. N. Morse and H. B. Arbuckle, correcting the results for the occluded gases in the oxide, obtained 65·46. H. Baubigny converted the anhydrous sulphate into oxide by calcination, and calculated 65·4 from the ratio $ZnSO_4$: ZnO. P. A. Favre dissolved a known weight of zinc in dil. sulphuric acid and burnt the resulting hydrogen to water. He calculated the at. wt. 65·99 from the ratios Zn : H_2 : H_2O. Like J. L. Gay Lussac, J. D. van der Plaats measured the vol. of the hydrogen evolved by treating a known weight of the metal with acid, and calculated the at. wt. 65·48 from the ratio Zn : H_2 ; H. C. Reynolds and W. Ramsay employed a similar method and obtained 65·78. J. W. Mallet likewise obtained 65·53. P. A. Favre ignited zinc oxalate, and weighed the resulting carbon dioxide ; he calculated the at. wt. 66·02 from the ratio ZnC_2O_4 : CO_2. J. C. G. de Marignac analyzed potassium

zinc chloride, K_2ZnCl_4, and obtained 65·29 and 65·33 for the at. wt. of zinc. J. H. Gladstone and W. Hibbert determined the amounts of copper and silver precipitated from soln. of the respective salts by a given amount of zinc, and from the ratio Zn : 2Ag, obtained 65·44 ; and from the ratio Zn : Cu, 65·65. L. Meaglia likewise precipitated silver and gold from soln. of their salts, and obtained respectively 65·485 and 65·436. T. W. Richards and E. F. Rogers obtained respectively 65·402 and 65·43 from the ratio $ZnBr_2$: 2Ag ; and 65·406 and 65·43 from the ratio $ZnBr_2$: 2AgBr. G. P. Baxter and M. R. Grose from the electrolysis of a soln. of zinc bromide with a mercury cathode obtained from the ratio Zn : Br_2, 65·388 ; and likewise from the ratio Zn : Cl_2, G. P. Baxter and J. H. Hodges obtained 65·38. A. L. Bernoulli calculated 65·569 for the at. wt. of zinc from thermodynamical data ; and W. M. Watts 64·78 from the period of vibration of the spectral rays. B. Brauner calculated 65·40 as the best representative value for the at. wt. of zinc ; F. W. Clarke computed 65·4182 with the probable error ±0·00048 ; and the International Table of at. wt. for 1920 gives 65·37 for the at. wt. of zinc. The **atomic number** is 30.

F. Stromeyer [4] determined the at. wt. of cadmium in 1818 by converting the metal into oxide by calcination, and calculated 111·49 from the ratio Cd : CdO. H. N. Morse and H. C. Jones, in 1892, converted a known weight of the metal into nitrate, and calcined the product for cadium oxide. They calculated the at. wt. 112·06 from the ratio Cd : CdO ; J. E. Bucher obtained at. wt. 112·08 and 111·87 when the nitrate was calcined respectively in porcelain and platinum dishes ; H. N. Morse and H. B. Arbuckle obtained 112·38. K. von Hauer converted the anhydrous sulphate into sulphide by heating it in a stream of hydrogen sulphide, and from the ratio $CdSO_4$: CdS calculated 111·94 for the at. wt. of cadmium ; E. A. Partridge likewise obtained 111·76 by converting the sulphate into sulphide, and 111·64 by converting the oxalate into sulphide, CdC_2O_4 : CdS. J. E. Bucher also obtained 112·11 from the ratio CdC_2O_4 : CdS. W. Blum converted the oxide into sulphide and calculated 112·69 from the ratio CdO : CdS. J. B. A. Dumas by titrating a soln. of a known weight of chloride with standard silver nitrate, obtained 112·31 from the ratio $CdCl_2$: 2Ag ; W. L. Hardin evaluated the ratio $CdBr_2$: 2Ag by electrolysis and computed 111·98 ; A. K. Huntington also computed 112·23 from the ratio $CdBr_2$: 2AgBr, and 112·24 from the ratio $CdBr_2$: 2Ag. J. E. Bucher computed 112·38 from the ratio $CdCl_2$: 2AgCl, and 112·39 from the ratio $CdBr_2$: 2AgBr. G. P. Baxter and M. A. Hines analyzed the chloride gravimetrically, and from the ratio $CdCl_2$: 2AgCl calculated 112·424 ; from the ratio $CdCl_2$: 2Ag obtained volumetrically, 112·409 ; G. P. Baxter, M. A. Hines, and H. L. Frevert likewise calculated 112·413 from the ratio $CdBr_2$: 2AgBr, and 112·421 from the ratio $CdBr_2$: 2Ag. E. A. Partridge obtained 111·80 from the ratio CdC_2O_4 : CdO ; H. N. Morse and H. C. Jones, 112·02 ; and J. E. Bucher, 111·88. W. S. Lorimer and E. F. Smith calculated the at. wt. 112·06 from the ratio CdO : Cd obtained by the electrolysis of a soln. of a known weight of the oxide in one of potassium cyanide. W. L. Hardin likewise calculated 112·06 from the ratio $CdCl_2$: Cd obtained by the electrolysis of a soln. of the chloride ; G. P. Baxter and M. L. Hartmann, from the ratio Cd : Cl_2 obtained 112·405 ; G. P. Baxter, M. R. Grose, and M. L. Hartmann, from Cd : Br_2 obtained 112·407 ; and G. P. Baxter and C. H. Wilson, from the ratio Cd : SO_4 obtained 112·409. J. E. Bucher converted cadmium into sulphate, and calculated 112·36 from the ratio Cd : $CdSO_4$. L. Meaglia precipitated gold from a soln. of sodium chloroaurate, and silver from a soln. of silver sulphate by means of cadmium, and from the two ratios calculated respectively 112·50 and 112·39. B. Brauner calculated 112·3 for the best representative value of the at. wt. of cadmium ; F. W. Clarke, 112·402 ± 0·0008 ; while the International Table for 1922 gives 112·40. The **atomic number** is 48. A. J. Dempster found that zinc consists of four **isotopes** of respective atomic weights—64, 66, 68, and 70. The relative intensities in the same order are 6 : 7 : 10 : 1. From these atomic weights of the isotopes and the proportions in which they occur in ordinary zinc, the atomic weight of the latter is calculated to be 65·5. F. W. Aston's experiment with cadmium

vapour was not successful, and the isotopes were not identified. A. C. Egerton obtained a partial separation of zinc by fractional distillation since the ratios of the sp. grs. of the two fractions to that of the original metal were respectively 0·99971 : 1 and 1·00026 : 1.

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§ 8. The Preparation of Zinc and Cadmium Oxides and Suboxides

When zinc is exposed to air at ordinary temp., it is soon covered with a thin grey film which protects the metal from further oxidation; molten zinc also rapidly oxidizes to a grey powder which soon forms the white oxide. J. J. Berzelius [1]

assumed that the grey powder is **zinc suboxide,** while H. Davy said: "The grey powder formed upon the surface of melted zinc, I am inclined to consider as a mixture of the white oxide with small particles of unburnt zinc." J. L. Proust, and A. Vogel also regarded it as a mixture of metal and oxide. R. C. Schüpphaus obtained a permanent canary-yellow powder by heating zinc oxide with carbon under press. The analysis showed that more zinc was present than corresponds to the normal oxide. It was also obtained by heating zinc oxide in vacuo, or in an atm. of purified nitrogen; or by heating a mixture of zinc oxide and zinc under press. This product was thought to contain a suboxide, but is more probably a soln. of finely divided zinc in the oxide. L. Meyer and F. Binnecker assumed that an unstable zinc suboxide is formed as an intermediate compound when zinc sulphate acts as a stimulant in the oxidation of sulphur dioxide; they applied a similar argument to **cadmium suboxide.**

R. F. Marchand [2] obtained a green powder by heating cadmium oxalate to the m.p. of lead. Mercury extracts no metal from the product, and when heated in air, it vigorously oxidizes, forming a mixture of the brown oxide and the metal. R. F. Marchand's analysis corresponded with **cadmium hemioxide,** Cd_2O. A. Vogel, however, regarded the product as a mixture of the metal and of the oxide, which contains a larger proportion of metal, the higher the temp. of decomposition. A. Souchay and E. Lenssen also support this view. F. Glaser found that acetic acid dissolves the oxide and leaves microscopic spherules of the metal; nor could he obtain any signs of the suboxide by reducing the oxide in a stream of hydrogen. M. S. Tanatar and M. Levin described a hemioxide, Cd_2O, or maybe Cd_3O_2, as a green powder which is produced by heating the basic oxalate, $CdC_2O_4.Cd(OH)_2$. It is said to be decomposed by water, and it apparently resembles the product obtained by R. F. Marchand. H. N. Morse and H. C. Jones prepared what they regarded as **cadmium subhydroxide,** or **cadmium monohydroxide,** CdOH, by washing one of the so-called subhalides with warm water at a temp. not exceeding 50°. The amorphous grey mass gives off hydrogen when treated with hydrochloric and sulphuric acids, but with nitric acid, nitric oxide is formed. When the dried product is heated to about 300° in a stream of nitrogen, a heavy yellow powder of cadmium hemioxide is formed in microscopic crystals. If the temp. exceeds 300°, it is said that the hemioxide decomposes into cadmium oxide and the metal. F. J. Brislee argued that cadmium hemioxide is the first product of the reduction of cadmium oxide. If the reaction $CdO \rightarrow Cd_2O$ is faster than the reaction $Cd_2O \rightarrow Cd$, there must be a break in the time-reduction curve corresponding with the existence of Cd_2O. The curve, Fig. 23, shows a distinct break corresponding to the reduction of cadmium oxide to the suboxide. M. S. Tanatar claimed to have made **cadmium quadrantoxide,** Cd_4O, by the cautious ignition of cadmium oxalate in a stream of dry carbon dioxide. It is a green, amorphous powder, which decomposes when treated with acids or ammonia into cadmium oxide and metallic cadmium. It is slowly decomposed by water, and is stable in dry air; its sp. gr. is 8·177 to 8·207 at 19°. When the suboxide is heated to the m.p. of cadmium in a current of carbon dioxide, it is converted into a yellowish-brown powder which is a mixture of metallic cadmium and cadmium oxide. Calorimetric measurements showed that the suboxide is not a mixture of cadmium oxide and cadmium, and it was concluded that the heat of formation of the suboxide, from cadmium oxide and the metal, is 7 Cals. H. G. Denham obtained a 5 per cent. yield of cadmium suboxide, Cd_2O, by M. S. Tanatar's and by H. N. Morse and

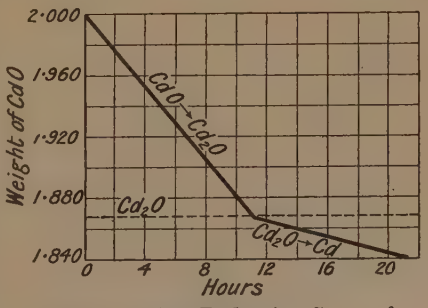

Fig. 23.—Time-Reduction Curve of Cadmium Oxide.

H. C. Jones' methods; he obtained a heterogeneous product containing cadmium and cadmium oxide by F. Glaser's and F. J. Brislee's methods.

The white powder which is deposited in the furnace outlets smelting zinciferous copper was known to the ancients. It is an impure zinc oxide, and probably contains arsenical oxides as well; its more modern equivalent is *tutty*. Dioscorides, in his *De materia medica* of the first century, mentioned two kinds, *pompholyx* and *spodium*. The former was white and light; the latter is blacker and heavier. He said:

> In the preparation and perfecting of brass, white pompholyx is made every time that the artificer sprinkles powdered cadmia upon the metal to make it more perfect. The very fine soot which rises is called pompholyx. Other pompholyx is made from cadmia by continual blowing with a bellows.

It is here probable that the zinc ore cadmia was reduced to metallic zinc which then burnt to the oxide. Hence pompholyx was Dioscorides' term for the white flowers of zinc, *flores zinci*, which he likened to wool, and which were for a time called *lana philosophica*—philosopher's wool. The flowers of zinc were collected in an apparatus, which recalls that now employed for collecting arsenic oxide. Dioscorides continued:

> The furnace is constructed in a two-storied building, and there is a medium-sized aperture opening to the upper chamber; the building wall nearest the furnace is pierced with a small opening to admit the nozzle of the bellows. The building must have a fair-sized door for the artificer to pass in and out. Another small building must adjoin this in which are the bellows and the man who works them. Then the charcoal in the furnace is lighted, and the artificer continually throws bits of cadmia from the place above the furnace, whilst his assistant, who is below, throws in charcoal, until all the cadmia inside is consumed. By this means, the finest and lightest part of the stuff flies with the smoke to the upper chamber, and adheres to the walls of the roof. The substance which is thus formed has at first the appearance of bubbles on water; afterwards increasing in size, it looks like skeins of wool. The heaviest parts settle in the bottom, while some fall over and around the furnaces, and some lie on the floor of the building. This latter part is considered inferior, as it contains a lot of earth, and becomes full of dirt.

Pliny, in his *Naturalis historia* of the first century, seems somewhat confused as to the difference between the two species *pompholyx* and *spodos*; and he applied the term *cadmia* to the mineral and to the flue-dust. G. Agricola [3] covers much the same ground as Dioscorides and Pliny. The product was used for medicinal purposes. Marcus Polo also described the method employed by the Persians for making pompholyx and spodos. The resemblance between the zinc oxide obtained by combustion and flakes of snow led the alchemists to term it *nix alba*; this term was mis-translated into German as *weisses Nichts*, and the latter, translated back to Latin, became *nihilum album*—*e.g.* I. Lawson, *Dissertatio de nihilo* (London, 1737). Flowers of zinc have also been called *tutia alexandrina*.

In 1810, A. Bruce [4] found a native manganiferous **zinc oxide,** ZnO, and he called it *red oxide of zinc*. G. Rose's, P. Berthier's, and A. A. Hayes' analyses pointed in the same direction; J. D. Whitney found samples of almost pure zinc oxide at New Jersey. R. Jameson, and C. C. Leonhard called it *prismatic zinc ore*; A. Breithaupt, *red zinc ore*; F. Alger, *stirlingite*; W. Haidinger, *zinkite*; and J. D. Dana, *zincite*. Analyses have also been reported by W. P. Blake, G. H. Stone, P. Grosser, J. A. Antipoff, G. L. Gorny, F. Rinne, H. Traube, A. Sachs, and J. T. Cundall. Crystallized zinc oxide was observed as a furnace product by J. F. L. Hausmann, A. Koch, A. Lévy, A. des Cloizeaux, J. J. Porter, F. C. Weber, G. Greim, K. Busz, W. V. Vernon, W. H. Miller, M. Delesse, J. W. Mallet, R. Cowper, H. Jordan, A. Laurent and C. Holms, F. C. Calvert, C. F. Rammelsberg, G. von Rath, H. Ries, L. Blum, and G. Rose. In 1901, E. Wittich and B. Neumann found crystallized **cadmium oxide,** CdO, occurring as *ein neues Cadmium-mineral* in the calamine mines of Iglesias (Sardinia).

Zinc oxide is produced when the metal is heated in air; the zinc takes fire when its temp. is high enough, part remains in the crucible, and part forms clouds of

oxide ; the surface of the metal should be stirred from time to time and the woolly mass removed so as to expose a fresh surface of metal. The product is rubbed up with water, and levigated to free it from adhering grains of metallic zinc. The resulting light flocculent powder forms the so-called flowers of zinc. If the temp. is not raised to the ignition point, the zinc furnishes the so-called grey suboxide, and finally the oxide. M. Rosenfeld [5] said that the presence of magnesium or sodium favoured the combustion of the metal. Zinc sulphate, nitrate, hydroxide, or carbonate also furnishes the oxide when calcined. This furnishes what was once called *zincum oxydatum via humida paratum*—zinc oxide prepared in the wet way. The carbonate is precipitated by adding an alkali carbonate to a soln. of a soluble zinc salt and well washing and drying the product. H. Brandhorst made the oxide by heating ammonium zinc carbonate. R. de Forcrand found zinc hydroxide is almost completely decomposed at 125°, and zinc nitrate at 300° for 2 hrs. H. Schulze calcined zinc chloride or iodide in a stream of oxygen ; V. Thomas found zinc iodide is converted into the oxide at ordinary temp. when exposed to nitrogen peroxide gas. C. Brunner calcined a mixture of zinc sulphate and sodium carbonate and extracted the mass with water ; J. Volhard calcined zinc chloride with mercuric oxide ; E. A. Parnell, and W. Hampe and C. Schnabel calcined a mixture of anhydrous zinc sulphate and carbon to about 650°. R. Alberti calcined a mixture of heptahydrated zinc sulphate with calcium or barium carbonate. G. E. Cassel extracted zinc from its complex ores with sulphurous acid under press., evaporating the soln. to dryness, and calcining the resulting zinc sulphite. When a soln. of sodium sulphate at 60° is electrolyzed between zinc electrodes with a current of 1000 amp. and 2·5 volts, zinc sulphate is formed at the anode, and this reacts with the sodium hydroxide formed at the cathode, producing zinc hydroxide. This is then washed, dried, and ignited.

G. C. Wittstein [6] recommended distilled zinc for the preparation of *flores zinci*. H. W. F. Wackenroder, F. P. Dulk, M. Horst, M. Veltzmann, and many others have dealt with the preparation of a highly purified zinc oxide *viâ humida paratum*. Commercial zinc oxide is also known as *zinc white—blanc de zinc, zinc weiss, snow white, Chinese white*, etc. It is largely used as a white pigment, and to a less extent in glazes and enamels. For many purposes, the physical character of the granules is of prime importance. For example, the covering power of zinc white when used as a paint is much greater when prepared by the combustion process, than when prepared by the ignition of the carbonate, etc. In France, the zinc or spelter is volatilized in a retort arranged so that the vapour is oxidized in a current of air, and the zinc oxide is collected in long settling chambers provided with hopper bottoms through which the collected oxide can be removed. In Silesia, and in America, the oxidized vapour is collected into large chambers with moistened upright canvas bags which permit the passage of flue gases, but arrest the oxide of zinc. J. Thomson, J. E. Booge, etc., have described processes for the preparation of zinc oxide.

Instead of oxidizing metallic zinc, several methods have been proposed for obtaining the oxide more directly from zinc ores. S. T. Jones,[7] for example, in 1850, and S. Wetherill, in 1855, worked with franklinite from New Jersey. The ore is conc. by magnetic separation ; mixed with about half its weight of anthracite coal, and possibly limestone ; and fed into a furnace. A blast of air is admitted to the furnace. The zinc is reduced to metal, volatilized, and then burnt with a dazzling white flame. The fume is drawn away by suction fans, and passes up a brick tower where the heavier and less pure particles of oxide separate out. The fume is then blown by means of fans to a cooling room, where more settling occurs. The cooled fume then passes to the bag rooms. The zinc oxide is afterwards graded according to colour and purity ; bolted through silk cloth ; and packed in barrels. Several other modifications of the process have been proposed. C. Kormorek recommended oxidizing the metal in a furnace like Bessemer's converter. A. O. Walker recommended the electrical precipitation of the dust of zinc oxide suspended in air.

Crystallized zinc oxide was prepared by A. C. Becquerel [8] in yellowish needles, by melting alkali hydroxide with powdered zinc oxide in a silver crucible. A. Daubrée obtained the crystals by passing the vapour of zinc chloride over lime; G. Brügelmann, by heating zinc oxide in a slow stream of hydrogen; H. V. Regnault, by passing steam over red-hot zinc; F. Fouqué and A. M. Lévy, by passing water vapour over red-hot zinc chloride; T. Sidot, by passing oxygen over the white-hot oxide; W. Florence, by fusing the oxide in borax; A. Gorgeu, by slowly heating a mixture of alkali and zinc sulphates; by heating zinc nitrate; or by fusing equal parts of potassium and zinc fluorides, and treating the resulting product with steam; H. Moissan, by subliming the oxide in the electric arc furnace; and V. Lepiarczyk, by heating to 1300°, a mixture of zinc sulphide and ferric oxide with exclusion of air.

The testing of zinc oxide for impurities and adulterations with barytes, etc., is a subject in analytical chemistry.[9] F. Fuchs and F. Schiff say the yellow colour is due to the presence of cadmium oxide; and they added that the blackening of zinc oxide on exposure to light is said to be due to the presence of zinc sulphide, and the blackening may be prevented by a thorough calcination. J. Cawley said the presence of magnesia hinders the blackening. W. W. Stoddart found traces of sulphate in commercial zinc oxide. F. O. Doeltz and C. A. Graumann say the carbonate in zinc oxide is derived by absorption of carbon monoxide from the air. R. Witte said pharmaceutical zinc oxide should not be made by calcining the nitrate, because, as H. N. Morse and J. White have shown, oxygen and nitrous gases are tenaciously occluded by the oxide prepared from the nitrate. T. W. Richards also noted the absorption of oxygen and nitrogen by ignited zinc oxide. Thus, a gram of zinc oxide at 660° lost 0·37 c.c. of gas; at 750°, 0·23 to 0·31 c.c.; and at 880°, 0·16 to 0·27 c.c. H. Pape removed lead oxide from zinc oxide by extraction with lime-water or milk of lime.

F. Stromeyer [10] noted that **cadmium oxide**, CdO, is formed when the metal is heated in air. H. V. Regnault also observed that the oxide is formed when cadmium is heated in contact with the vapour of water; if a current of steam is passed over the heated metal, the latter volatilizes below the temp. of the reaction. P. Sabatier and J. B. Senderens found that at 300°, finely divided cadmium is gradually oxidized by nitrous oxide; the metal simultaneously volatilizes. J. A. Wilkinson obtained the oxide by the action of sodium peroxide on molten cadmium. C. Poulenc prepared the oxide by melting cadmium fluoride with alkali carbonate; E. F. Smith and P. Heyl, by heating a mixture of cadmium chloride and mercuric oxide; and J. E. Bucher, by the calcination of the oxalate. W. S. Lorimer and E. F. Smith precipitated the carbonate by adding ammonia and ammonium carbonate to a soln. of cadmium nitrate; the precipitate was thoroughly washed with cold water, dried, and then ignited. The oxide is also obtained by heating the hydroxide, nitrate, etc. G. Werther found crystals of cadmium oxide in the distillation vessel of a Silesian zinc retort. W. Florence obtained crystals by fusing the oxide with borax; and E. Wittich and B. Neumann obtained crystals of cadmium oxide as a sublimate by heating the metal in oxygen. E. Schüler, and T. Sidot prepared crystals by heating the oxide while hot in a stream of oxygen. W. Herapath also obtained crystals of the oxide by heating the metal in a stream of air, in a glass tube.

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§ 9. The Properties of Zinc and Cadmium Oxides

The **colour** of native zinc oxide varies from dark red to blood-red which in thin plates is dark yellow ; the pigment is attributed to the presence of manganese oxide as an impurity. The artificial oxide appears as a white flocculent mass which acquires a yellow tinge when the temp. is raised, but the white colour is restored on cooling. According to A. Vogel,[1] the change is not connected with either the evolution or absorption of oxygen. The yellow tint sometimes exhibited by the artificial oxide is considered to be due to the presence of foreign oxides—*e.g.* F. Fuchs and F. Schiff said cadmium—but E. Jensen regarded it as characteristic of the oxide prepared by precipitation and ignition. H. W. F. Wackenroder stated that the dense oxide precipitated from hot soln. and containing traces of sodium chloride or sulphate is not yellow, whereas the higher oxide precipitated from hot soln. and afterwards ignited, has a yellow tinge when cold. R. de Forcrand noted that the crystalline powder obtained by heating the nitrate to 350° has a greenish-yellow tinge. R. Schindler said that the yellow oxide loses its coloration after it has been strongly ignited on platinum. W. Herz and E. Diesel made a similar observation. J. Tafel found purified and dry colourless zinc oxide is coloured brown by strongly rubbing, by press., or by exposure to canal or cathode rays ; the colour is removed by strong calcination. Cadmium oxide varies from a yellowish-brown to a brownish-red, purple-red, dark brown, or bluish-black powder. K. Bädeker oxidized the film of metal obtained in a glass discharge tube near the cathode, and found it to be orange-yellow at ordinary temp., and brown when hot. He says that under the microscope, the layer is a continuous film. According to H. Laspeyres, the crystals of zincite have a feeble **pleochroism**. R. Whytlaw-Gray and co-workers studied the aerosols or smokes of zinc and cadmium oxides.

V. Kohlschütter and J. L. Tüscher found that zinc and cadmium oxides can be obtained in a highly disperse form by vaporizing the metals in an electric arc ; suddenly chilling by a current of cold air ; and precipitating the fume by means of a high tension electric field. Zinc oxide, zincite, or red zinc ore forms hexagonal bipyramidal **crystals** which, according to H. Traube, have the axial ratio $a : c = 1 : 6077$. The forms of the crystals have also been studied by J. Antipoff, G. T. Prior, H. G. F. Schröder, A. Lévy, J. Schabus, F. Rinne, G. Greim, K. Busz, G. Cesaro, A. Hutchinson, H. Ries, A. Sachs, J. F. L. Hausmann, A. des Cloizeaux, P. Grosser, and F. Sandberger. Cadmium oxide crystallizes in the cubic system ;

T. Sidot's oxide is in the form of small cubes; both H. Moissan, and G. Brügelmann obtained hexahedral crystals; and A. Ditte, and E. Schüler obtained needle-like crystals or octahedral forms; C. Poulenc, brown plates; and E. Schüler, a dark bluish-black powder of microscopic octahedra. Similar forms were observed by K. von Hauer, G. Brügelmann, and B. Neumann and E. Wittich. G. Werther obtained combinations of tesseral octahedra and icositetrahedra, and of cubes and dodecahedra. W. L. Bragg showed that **X-radiograms** of zinc oxide indicate that the zinc atoms are arranged on two hexagonal space-lattices with their centres corresponding closely with those of a set of equal spheres in hexagonal close packing. The corresponding axial ratio is $a : c = 1 : 1{\cdot}632$, while the observed value is $1 : 1{\cdot}6077$. The positions of the atoms are identical with those of the hexagonal close-packed arrangement of spheres if the latter be supposed to contract in the direction parallel to the hexagonal axis so as to reduce the $c : a$ ratio from 1·632 to 1·6077. The oxygen atoms are probably on two hexagonal space-lattices identical with those on which the zinc atoms are situated, and derived from the latter by a movement of translation parallel to the c-axis. This brings every oxygen atom into the centre of four zinc atoms arranged at the corners of what is very nearly a regular tetrahedron. This is illustrated in Fig. 24, where the black spots indicate zinc atoms, and the circles, oxygen atoms. G. Aminoff, and W. L. Bragg computed that the elementary parallelopiped has sides $a = 3{\cdot}22$ A. and $c = 5{\cdot}20$ A. J. A. Hedvall, and G. Aminoff studied the X-radiogram of zinc oxide; and W. P. Davey and E. O. Hoffman that of cadmium oxide. W. P. Davey found that cadmium oxide exhibits the simple cube lattice with sides 4·61 A., and the closest approach of the atoms, 2·30 A. M. L. Huggins made observations on this subject. F. Rinne studied the **corrosion figures**; and H. Traube the **pyro-electricity** of crystals of zincite.

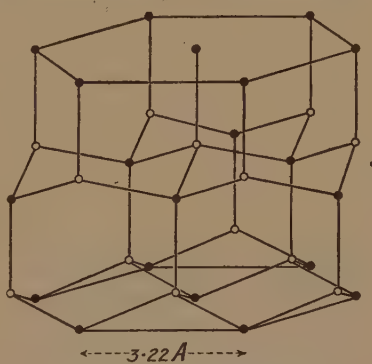

FIG. 24.—W. L. Bragg's Space-lattice of Zinc Oxide.

The reported numbers [2] for the **specific gravity** of zinc oxide range between R. Böttger's 5·432, and C. J. B. Karsten's 5·7344; H. G. F. Schröder's mean is 5·65. In addition, G. Brügelmann gave 5·47 at 15° for the amorphous oxide, and 5·782 at 15° for the crystalline oxide. W. P. Blake's value for zincite is 5·684; and E. Madelung and R. Fuchs', 5·5783 (0°). C. J. B. Karsten gave 6·9502 for the sp. gr. of cadmium oxide; W. Herapath, 8·183 at 16·5°; and G. Werther, 8·1108. The **hardness** of zincite is between 4·0 and 4·5; that of cadmium oxide crystals is about 3·0. A. Reis and L. Zimmermann have discussed this subject. E. Madelung and R. Fuchs gave $0{\cdot}77 \times 10^{-6}$ megabars per sq. cm. for the **compressibility** of zincite.

H. Fizeau [3] gave $\alpha = 0{\cdot}00000316$ for the **coefficient of thermal expansion** of zinc oxide, and H. Kopp gave $\alpha = 0{\cdot}000004$ for the coeff. of linear and 0·000016 for the coeff. of cubical expansion. H. V. Regnault gave 0·1248 for the **specific heat** of zinc oxide between 17° and 98°; measurements at a low temp. were made by A. Magnus. The oxides of zinc and cadmium are highly refractory towards heat. R. Cusack gave 1260° for the **melting point** of red zinc ore. H. Pape found that the oxide sintered before it fused.

The **volatility** of zinc oxide is marked at a white heat. T. Sidot [4] also reported the volatility of cadmium oxide at a white heat. R. de Forcrand said that no volatilization or dissociation occurs at a bright red heat; nor did A. A. Read detect any change when zinc or cadmium oxide is heated to the m.p. of platinum. H. Hasenclever and C. Stahlschmidt found that zinc oxide begins to volatilize at about 970°, and at 1054° it lost 16·9 to 17·8 per cent. in weight when heated for 30 mins.

in a stream of carbon monoxide. The oxide made by roasting zinc blende does not volatilize appreciably at 970°, but does so at 1054°. F. O. Doeltz and C. A. Graumann obtained rather lower values for the volatility of zinc oxide. They said that the volatilization is inappreciable at 1000°, but begins at 1200°; at 1300°, the oxide loses about one per cent.; at 1400°, 13 per cent.; and at 1700°, the volatilization is very rapid. They added further that some reports of loss by volatilization when zinc oxide is calcined in air may be really mal-observations due to the expulsion of a little absorbed carbon dioxide; and that the oxide which has been calcined in air for an hour at 1000°, loses 0·06 to 0·09 per cent. when recalcined for 2 hrs. at the same temp.; and the oxide which has been calcined four times at 1000°, loses 0·14 to 0·18 per cent. when again calcined at 1200° for 2 hrs. O. L. Kowalke reported that zinc oxide may be completely volatilized between 1370° and 1400°. F. O. Doeltz and C. A. Graumann noted that cadmium oxide volatilizes below 1000°. J. C. G. de Marignac, and A. Erdmann observed that when zinc oxide is heated in a platinum crucible by a gas-flame, a film is formed on the inside, and the former assumed that the zinc oxide is dissociated and that the zinc alloys with the platinum; but H. N. Morse and W. M. Burton said that reducing gases pass through the metal crucible and by reducing the oxide liberate the metal, which then alloys with the platinum. H. St. C. Deville and L. Troost sublimed zinc oxide in a stream of hydrogen, and concluded that the oxide is first reduced by the hydrogen, forming water, and that the metal is then oxidized by the water, reforming the oxide. No sublimation occurred in a stream of inert gas. H. N. Morse and J. White at first attributed the apparent volatilization to alternate reduction and oxidation of zinc oxide when heated in a stream of hydrogen. They found the oxide does not sublime when heated in vacuo, but it does so when heated with zinc. Later, they attributed the apparent volatilization of zinc oxide from a mixture of the metal and the oxide to the mechanical transport of particles of the oxide with the zinc vapour, for they found that powdered porcelain, or barium carbonate, is similarly transported without change of composition. Similar remarks apply to cadmium oxide. H. Moissan obtained a sublimate of needle-like crystals of the oxide in the electric-arc furnace. C. Zenghelis claimed to have obtained evidence of the volatilization of zinc oxide at ordinary temp. W. Stahl estimated the **dissociation pressure,** p atm., of zinc oxide to be:

	227°	1227°	1727°	2227°	2727°	3227°	3427°	3527°	3627°
p	$0{\cdot}0_{66}1333$	$0{\cdot}0_{16}3620$	$0{\cdot}0_{10}9489$	$0{\cdot}0_{6}7358$	$0{\cdot}0_{3}3057$	0·02365	0·09784	0·1885	0·3517

and the dissociation press. of the oxide is equal to the partial press. of atm. oxygen at 3544°. According to A. Colson, cadmium oxide dissociates below 600°, and the volatilized film of cadmium forms in transmitted light a violet-blue film on the walls of the glass vessel.

J. Thomsen [5] gave the **heat of formation** of zinc oxide (Zn, O) as 85·43 Cals.; C. M. Despretz, 85·00 Cals.; M. Berthelot, 85·40 Cals.; P. L. Dulong, 84·408 Cals.; T. Andrews, 86·90 Cals.; P. A. Favre and J. T. Silbermann, 84·50 Cals.; T. Woods, 85·50 Cals.; and M. Délepine and L. A. Hallopeau, 84·80 Cals. R. de Forcrand gave for the heat of formation of zinc oxide, prepared from the nitrate at 125°, 82·97 Cals.; and prepared from the nitrate at 350°, 83·00 Cals. A. Ditte also found different values for the heat of formation of the oxide which has been calcined at different temp., as shown by the heat of soln. in dil. sulphuric acid, but J. C. G. de Marignac failed to confirm this observation. The results per gram of zinc oxide, calcined at:

	J. C. G. de Marignac.	A. Ditte.
350°	261	244·2 cals.
Dull redness	266	272·0 „
Bright redness	264	299·3 „

R. de Forcrand gave for the heat of soln. in dil. sulphuric acid, 25·24 Cals. for zinc oxide obtained by calcining the hydroxide at 125°; 25·21 Cals., by calcining the

nitrate at 350°; 23·91 Cals., by calcining at bright redness the precipitated hydroxide; and 23·51 Cals., by the combustion of zinc. Precipitated zinc hydroxide has a heat of soln. in dil. hydrochloric acid of 20·23 Cals. A. Ditte also found that the heat developed in the soln. of a gram of cadmium oxide, obtained by calcining the nitrate, in dil. sulphuric acid, containing 382·5 grms. H_2SO_4 per litre, is 229·6 cals., or 14·238 cals. per eq.; while the heat developed from the oxide obtained by the combustion of cadmium, or the calcination of the carbonate, is 234·1 cals. per gram, or 14·513 cals. per eq. W. Herz was unable to establish the existence of allotropic forms of zinc oxide. G. Bodländer calculated the free energy of the reaction $Zn+\frac{1}{2}O_2=ZnO$ to be $85800-30·8T+2·29T \log p$ cals. per mol, where p is the press. of the oxygen in the atm. M. Berthelot gave 66·4 Cals. for the heat of formation of cadmium oxide; J. Thomsen, 65·78 Cals.; and W. Müller-Erzbach gave 65·6 Cals. A. Ditte gave (Cd, O), 60·8 Cals., and for the transformation of amorphous into crystalline cadmium oxide, 0·540 Cal. R. de Forcrand, and N. von Klobukoff also measured the thermal effect in passing from the amorphous to the crystalline state. J. Thomsen found for the **heat of neutralization** of zinc hydroxide $Zn(OH)_2+H_2SO_4$ aq., 23·41 Cals.; $Zn(OH)_2+2HNO_3$ aq., 19·83 Cals.; $Zn(OH)_2+2HCl$ aq., 19·88 Cals.; and $Zn(OH)_2+2CH_3COOH$ aq., 18·03 Cals. A. Ditte, and M. Berthelot measured the heat of neutralization of cadmium oxide in dil. sulphuric acid; and J. Thomsen found [Zn, O, H_2SO_4 aq.]=106·09 Cals. J. Thomsen gave for the heat of neutralization [$Cd(OH)_2$, 2HCl, H_2O], 20·29 Cals.; [$Cd(OH)_2$, 2HBr, H_2O], 21·56 Cals.; and [$Cd(OH)_2$, 2HI, H_2O], 24·21 Cals.; [Zn, O, $2HNO_3$, aq.], 102·51 Cals. The **heat of hydration** of zinc oxide, according to J. Thomsen, is [Zn, O, H_2O], 82·68 Cals.; [ZnO, H_2O], —2·75 Cals.; and for cadmium oxide [Cd, O, H_2O], 65·68 Cals., or [CdO, H_2O], —0·10 Cal.

According to A. des Cloizeaux,[6] the crystals of zincite have a positive **double refraction,** and the subject has been investigated by G. Cesaro, A. Breithaupt, and A. Madelung. W. W. Coblentz[7] found that zincite had a poor reflecting power, and the selective reflection **spectrum** exhibited no bands; he also examined the **emission spectrum** of the heated oxide, and found a uniform distribution of energy in the infra-red, with a depression in the emissivity wave-length curve at 3·2μ. Zinc oxide emits an intense light when heated in the blowpipe flame. T. Drummond found that if used in place of lime for the limelight, the intensity of the light was less than that of magnesia, and the oxide rapidly wasted away. The **thermo-luminescence** of zinc oxide above 880° has been studied by E. L. Nichols and B. W. Snow. E. L. Nichols and D. T. Wilber found that, like calcium oxide, zinc oxide exhibits **flame luminescence.** E. L. Nichols showed that pure zinc oxide does not exhibit photo-luminescence, nor is it excited by X-rays; but it is luminescent above red heat—a red band appearing at about 568°, and at 700° this is displaced by a yellowish-green band which disappears about 940°. Cadmium oxide gave no flame phosphorescence. According to E. L. Nichols, at 1000°, in the oxyhydrogen flame, zinc oxide appears blue, not red. According to W. Wien, zinc oxide gradually loses its fluorescent qualities in the **canal rays,** and at the same time acquires a yellow colour, and, according to J. Tafel, is denser. According to H. Jackson, the fluorescence of purified zinc oxide also occurs under the influence of the **cathode rays.** J. Ewles found the minimum voltage for the excitation of the cathodo-luminescence to range from 400 to 850 with different samples of zinc oxide. The rays of radioactive bismuth—polonium—were found to give an intense phosphorescence with zinc oxide. According to W. Wien, the canal ray fluorescence is not exhibited by zinc oxide prepared from the hydroxide precipitated with sodium carbonate. J. A. Wilkinson examined the luminescence of cadmium oxide, and cadmium salts. E. Wiedemann and G. C. Schmidt also found the intensity of the luminescence to be dependent on the acid radicle. G. C. Schmidt attributes the yellow or yellowish-green **fluorescence** of zinc oxide to traces of cadmium; when the latter is removed by fractional distillation, the oxide does not fluoresce. E. Goldstein found the presence of 0·0000001 part of foreign metal to be effective in the production of the

cathodic luminescence. When zinc oxide preparations are illuminated with **ultra-violet rays,** a luminescence is displayed which increases to a maximum, and on removing the exciting rays, the luminescence disappears, but a weak and transient phosphorescence appears. The wave-length of the luminescence is in the region 300–313$\mu\mu$. A. Karl found that a calcined mixture of zinc oxide with silicic, stannic, titanic, or zirconium oxide, praseodymium oxide, manganese nitrate, silicate, stannate, titanate, or zirconate readily shows **tribo-luminescence,** giving a glow visible in daylight, when rubbed with a metal or glass rod. It is assumed that solid soln. are formed. Manganiferous zinc sulphate or nitrate is also triboluminescent. According to G. C. Schmidt, a solid soln. of cadmium and zinc oxide is not formed by the combustion of cadmiferous zinc, but is formed when the mixture is calcined; and the luminescence is said to be connected with the decomposition of the salt or oxide. According to H. Maraoka and M. Kasuya, zinc or cadmium oxide blackens a **photographic plate.** C. Winther found that some varieties of zinc oxide act as optical sensitizers in a number of processes without being changed—*e.g.* white lead and glycerol mixtures do not turn black in daylight or in the electric arc, but they blacken if zinc oxide is present; and oxygen is converted to ozone, provided zinc oxide be present, when exposed through glass to light from a quartz mercury lamp.

According to F. Beijerinck,[8] and O. Frölich, zincite is an electrical conductor, and its **electrical conductivity** is greater perpendicular to the principal axis than it is parallel to that axis. J. Sohlmann noted the relatively high conductivity of zinc oxide when it is heated by the oxy-hydrogen flame, or by the electric arc; and below 1000° it begins to conduct better than the oxides of calcium, beryllium, or magnesium. M. Lapschin and M. Tichanowitsch reduced zinc oxide to the metal by a battery of 60 to 370 Bunsen's cells. C. A. Kraus found the sp. conductivity of cadmium oxide to be $0{\cdot}083\times10^{-4}$ mho. A. A. Sommerville found that a column of zinc oxide, 1 cm. diameter and 10 cms. long, had an **electrical resistance** of 10^7 ohms at 393°, and 72 ohms at 1100°. The electrical conductivity of zinc oxide was found by F. Skaupy to be greater in vacuo than in air. With a direct current of 110 volts, at a press. of 0·01 mm. of mercury, 2–3 milliamps. passed through the oxide, but in a few seconds this increased to 100–500 milliamps. There was no evolution of oxygen. F. Skaupy suggested the use of zinc oxide for a resistance with a negative temp. coeff., and for non-corrosive electrodes in vacuum tubes. F. Streintz found that the conductivity of the strongly compressed powder of cadmium oxide does not change one per cent. when kept 14 days. Increasing the press. or lowering the temp. down to that of liquid air, has no influence on the conductivity. The specific resistance amounts to 280×10^{-4} ohms. A rod 2·3 cms. long and 0·229 cm. diameter has a resistance of 1·2 ohm between −180° and 200°; above 200°, the resistance decreases rapidly so that at 300° it is 0·26 ohm, and at 400°, 0·11 ohm; and when cooled to the temp. of the room, the resistance is only 0·06 ohm. The resistance, R, changes with the temp. $\theta°$, so that $R=0{\cdot}0055(1+0{\cdot}001\theta)$. F. Streintz assumes that above 200°, a poor conducting variety of cadmium oxide changes into a good conductor. S. Veil found that the curve showing the variation in the conductivity of cadmium oxide with temp. has three points of inflexion which are assumed to represent α-, β-, and γ-allotropic forms of the oxide. K. Bädeker measured the conductivity of films of cadmium oxide on glass; and he found the **thermo-electromotive force** of copper or silver against cadmium oxide is 30·0 microvolts per degree between 18° and 100°, and 40·0 microvolts between 100° and 180°.

Zinc oxide was observed by J. Perrin to be feebly positive in neutral water, and strongly positive in acidified water. R. Lorenz found the potential of zinc in contact with oxygen, against a normal hydrogen electrode in neutral soln. to be −0·31 volt. L. Bloch measured the **contact difference of potential** of zinc oxide against distilled water=1 volt; against N-H_2SO_4, or N-HCl, 1·2 volt, and with more dil. soln., the potential decreases; the difference of potential against alkaline soln. is smaller than for water, and against salt soln. the value is nearly the same as for water.

R. Lorenz and H. Hauser found the e.m.f. of the cell $Cd|O_2$, N-NaOH, $H_2|Pt$ to be 0·411 volt at 18·4°, and 0·308 volt at 30°; while the e.m.f. of the cell $CdO|O_2$, N-Na_2SO_4, $H_2|Pt$ is 0·069 volt. S. Glixelli studied the **electro-osmosis** of zinc oxide. S. Meyer found the **magnetic susceptibility** of powdered zinc oxide to be $-0·26\times10^{-6}$ units at 16° (air unity); C. Chéneveau gave $-0·33\times10^{-6}$ units. E. Thomson [9] has investigated the orientation of fine particles of zinc and cadmium oxides in the magnetic field.

T. W. Richards and E. F. Rogers [10] have shown that zinc oxide prepared by the ignition of the nitrate always carries **occluded gases,** —1·0 to 15 c.c. of gas per 10 grms. of oxide; the gas consisted mainly of **oxygen** and **nitrogen** with a trace of carbon dioxide. The oxide derived from the carbonate contained rather more carbon dioxide. Cadmium oxide contained only a trace of occluded gas. H. N. Morse and H. B. Arbuckle obtained oxygen and nitrogen from ignited zinc and cadmium oxides. C. M. Despretz,[11] and H. W. F. Wackenroder observed the great difficulty in reducing zinc oxide by **hydrogen.** H. St. C. Deville showed that with a slow current of gas and a wide porcelain tube, crystalline zinc oxide is alone produced, but with a fast current of gas and a narrow porcelain tube, the oxide is reduced. He assumed that reduction probably occurs in both cases, and he considered that the effect is not due to mass action. He said:

> At the moment when the steam and zinc react to reproduce zinc oxide, and hydrogen, the latter gas, by reason of its mass, should protect the metal from oxidation. This never happens if the operation is conducted with sufficient slowness. All is explained, however, by admitting that a variation of temp. causes the affinities to be reversed. Thus, in the part of the tube heated directly, zinc vapour and steam may coexist; but in the parts less heated, where the zinciferous deposit occurs, the affinities change, water is decomposed, and every trace of metallic zinc disappears. This takes place in my experiments; but when the hydrogen passes with rapidity, the zone of the tube in which the reverse action occurs is traversed by the mixture of vapours with such rapidity that the cooling prevents the reversal of the reaction.

H. St. C. Deville's experiments were confirmed by J. Percy, and it is more probable that the reversible reaction: $ZnO+H_2\rightleftharpoons H_2O+Zn$, is involved in both cases, and that with a fast current of hydrogen the zinc vapour is carried along and condensed before the reverse reaction has time to progress very far. According to F. Glaser, hydrogen reacts slowly with zinc oxide at 454°; and after heating for an hour at 600°, 1·25 per cent. of metal is volatilized, and after heating for another hour at 670°, about half the metal had sublimed. W. Kumpmann stated the reduction of zinc oxide by hydrogen begins at about 465°, and no metal or suboxide is produced with a slow current of gas at from 700° to 1000°. The more rapid the current of gas the more zinc oxide sublimes, and some metal may be obtained as a fine dust at 500° or even lower. F. Glaser found that the reaction between hydrogen and cadmium oxide begins at about 282° and the reduction is complete in 3 hrs. between 290° and 300°. W. Müller found the reduction of cadmium oxide by hydrogen begins between 250° and 260°, and is quite fast at 270°; accordingly he recommended this reaction as a means of separating cadmium and copper oxides; and L. C. Barreswil, as a means of separating zinc and cadmium oxides; R. E. Wilson and T. Fuwa studied the hygroscopicity of zinc oxide.

According to H. Moissan,[12] **fluorine** does not attack cold zinc oxide, but near 500° decomposition takes place; and C. Poulenc found that **hydrogen fluoride** forms cadmium fluoride when passed over red-hot cadmium oxide. R. Weber obtained zinc or cadmium chloride and oxygen by passing **chlorine** over the red-hot oxide. Zincite is readily soluble in dil. **acids**—dil. hydrochloric, sulphuric, acetic, and nitric acids. These acids also dissolve cadmium oxide. G. J. Fowler and J. Grant observed that zinc oxide has no effect on the decomposition of **potassium chlorate** by heat. H. Brandhorst found zinc oxide to be soluble in molten zinc or magnesium chloride. W. Bersch studied the action of cadmium oxide on soln. of the **chlorides, bromides, and iodides of the alkalies and alkaline earths.**

Zinc oxide is decomposed by the vapour of **sulphur** forming zinc sulphide and

sulphur dioxide. E. Aston and L. Newton,[13] contrary to C. R. Fresenius, were unable to convert zinc oxide quantitatively into zinc sulphide by admixture with sulphur, and heating in a current of hydrogen—from 5 to 15 per cent. escaped conversion—even after repeated treatments. J. B. Senderens found zinc oxide is not affected by boiling it with water and sulphur, while cadmium oxide forms the sulphide, sulphate, and a little thiosulphate. H. Moissan observed that a soln. of **ammonium sulphide** converts zinc oxide into orange-yellow crystals. H. Schiff detected no action between **sulphur dioxide** and zinc oxide or zinc sulphide ; and E. Priwoznik found that at ordinary temp. a soln. of ammonium polysulphide converts cadmium oxide completely into the sulphide. C. Matignon and F. Bourion found the vapour of **sulphur chloride,** S_2Cl_2, passed with a stream of chlorine over red-hot zinc oxide, produced zinc chloride. F. Faktor fused zinc oxide with **sodium thiosulphate,** and found that sulphur dioxide is evolved, and zinc sulphide formed. V. Lepiarczyk reported that when a mixture of zinc oxide, carbon, and **calcium sulphate** is heated to about 1300°, zinc sulphide is formed ; W. Mostowitsch obtained a similar result with **barium sulphate** at about 800°. The action of **sulphuric acid** on cadmium and zinc oxides has been previously indicated. P. Sabatier found zinc oxide reacts vigorously with **nitrosyldisulphonic acid,** $NO(HSO_3)_2$, forming zinc sulphate.

C. H. Burgess and A. Holt [14] found zinc and cadmium oxides dissolve to a clear glass in molten **boric oxide.** J. Percy likewise found zinc oxide dissolves in fused boric acid in the proportions $ZnO : B_2O_3$, 1 : 1, 2 : 1, 3 : 1, and 4 : 1, forming transparent glasses ; and with a mixture of zinc oxide and **alumina,** at a high temp., he obtained a " compact, grey, strong substance which scratched flint glass "—*vide* the aluminates. When cadmium oxide is heated with **phosphorus,** B. Renault found that cadmium phosphide is formed. H. Hvoslef likewise obtained zinc phosphide by the action of phosphorus vapour on zinc oxide. F. Ephraim heated cadmium oxide with **sodium amide** in a sealed glass tube, and obtained beads of cadmium.

When a mixture of zinc oxide and **carbon** is heated to a bright redness, zinc vapour and carbon monoxide are produced ; and if the zinc oxide is in excess, carbon dioxide is also formed—*vide* the extraction of zinc. O. Boudouard,[15] and W. Mostowitsch detected signs of the reduction of zinc oxide by carbon at 800°, and F. O. Doeltz and C. A. Graumann between 800° and 1000°. W. Kumpmann found the reduction commences at a temp. over 1000°. W. McA. Johnson gave 1022° with wood charcoal, and 1029° with coke ; E. Prost gave 1075°. M. Bodenstein and F. Schubart found the velocity, v, of the reaction between zinc oxide and carbon at different temp., measured in terms of loss in weight per gram per min. to be :

	990°	1000°	1016°	1030°	1039°
v . . .	0·050	0·058	0·156	0·180	0·180
$dv/d\theta$ . .	0·0008	0·0061	0·0017	0·0000	

According to O. Boudouard, the evolution of gas which commences at 800°, ceases as the temp. rises, and again commences at about 1100°, and between 1125° and 1150°, there is a regular stream of gas which contains about 99 per cent. carbon monoxide and 1 per cent. of carbon dioxide. Zinc oxide prepared artificially is more easily reduced than that obtained by roasting the sulphide. K. Eichhorn, F. Fischer, and W. Hempel have studied the reduction of zinc oxide by carbon ; the latter said the reaction starts below the b.p. of zinc, and is complete between a bright red and a white heat. According to R. C. Schüpphaus, the reduction of zinc oxide by carbon commences at 910°, and when the press. is maintained above the calculated press. of zinc vapour, at 1150°, liquid zinc collects as an ingot at the bottom of the crucible, although the temp. is higher than the b.p. of zinc under atm. press. A stable canary-yellow oxide is produced which contains more zinc than corresponds with the normal oxide, and which may be a suboxide (*q.v.*). F. O. Doeltz and C. A. Graumann found that the reduction of cadmium oxide by sugar carbon is very slow

between 530° and 620°—relatively 0·1 per cent. loss of weight was observed ; there was an abrupt acceleration as the temp. rose in the vicinity of 700°, and relatively 1·0 per cent. loss of weight occurred.

Zinc is directly extracted nearly always from a mixture of zinc oxide and some form of carbon. The two are often in the form of coarse particles and but imperfectly mixed. Contact between the solids is therefore imperfect, and yet the reduction is virtually complete. Hence, argued F. le Play, **carbon monoxide** alone must be the reducing agent ; he extended the hypothesis and assumed that solid carbon does not reduce oxides by direct contact. While admitting that carbon monoxide can reduce the oxides of the metals, J. L. Gay Lussac pointed out that it does not follow that solid carbon is incapable of reducing oxides by direct contact. The more easily reducible oxides—silver, mercury, copper, lead, bismuth, etc.—are reduced by carbon monoxide forming carbon dioxide. There are also oxides—manganese, chromium, cerium, titanium, and potassium—which resist the action of carbon monoxide, and are yet reducible by carbon. F. Clément and J. B. Désormes, P. L. Dulong, C. M. Despretz, and A. Müller early noted the difficulty in reducing zinc oxide with carbon monoxide, and I. L. Bell reported that zinc oxide is not changed when heated with carbon monoxide in a sealed tube. According to W. Kumpmann, similar remarks apply to carbon monoxide as were made with respect to the action of hydrogen on heated zinc oxide. F. O. Doeltz and C. A. Graumann found the reaction begins between 800° and 1000° ; W. Kumpmann obtained signs of the beginning of the reaction at 465° ; and it is appreciable between 700° and 800°. The relations between carbon monoxide and dioxide, zinc, and zinc oxide have been indicated in connection with the extraction of zinc. The reversible reaction is symbolized : $ZnO+CO \rightleftharpoons CO_2+Zn$; the carbon dioxide produced in the action of carbon on zinc oxide has no chance to reoxidize the zinc because, in the presence of excess of carbon, it is reduced to carbon monoxide, so that as long as sufficient red-hot carbon is present, zinc and carbon monoxide are the sole products of the reactions. W. Kumpmann found that zinc oxide sublimed unchanged in a mixture of 90 vols. of **carbon dioxide** and 10 of carbon monoxide ; and from a mixture of carbon and zinc oxide in a stream of carbon dioxide at 700° ; or a stream of steam at 800°. Zinc oxide attracts carbon dioxide from the air ; brown cadmium oxide behaves similarly and becomes white.

A. Mailhe [16] found zinc oxide decomposes methyl alcohol into equal parts of hydrogen and carbon monoxide. W. Ipatjeff, and P. Sabatier and A. Mailhe found ethyl alcohol vapour is decomposed by zinc oxide ; some aldehyde is formed ; and at 340°–350°, a gas with 95 per cent. hydrogen and 5 per cent. of ethylene is produced. A. Mailhe found fatty acid vapours form ketones and carbon dioxide at about 400° ; thus, at 430°, acetic acid forms acetone. Analogous results were obtained with cadmium oxide. W. G. Palmer studied the catalytic action of zinc oxide admixed with cupric oxide on the dehydrogenation of ethyl alcohol.

F. von Kügelgen [17] reduced red-hot zinc oxide by **calcium carbide**. P. Berthier, and J. Percy fused zinc oxide with **alkali carbonate** and obtained a liquid which congealed to a colourless, translucent, crystalline mass ; fused **potassium cyanide** dissolves zinc oxide without showing any signs of the vaporization of reduced zinc. W. Bersch investigated the action of soln. of the alkali and alkaline earth **thiocyanates** on cadmium oxide ; and J. Milbauer found that zinc oxide is converted into amorphous zinc sulphide by potassium thiocyanate at about 220° ; similar results were obtained with cadmium oxide. J. Percy found mixtures of zinc oxide and **silica** $ZnO : SiO_2$, in the proportions 1 : 1, 2 : 1, 3 : 1, and 4 : 1 sintered together after five hours at a white heat—*vide* the silicates. G. Rauter found **silicon tetrachloride** is decomposed by zinc or cadmium oxide between 290° and 300°.

Zinc oxide is reduced by less easily reducible metals—*e.g.* by **potassium** at a gentle heat ; A. Burger [18] reduced zinc and cadmium oxides by **manganese** ; A. Stavenhagen and E. Schuchard, by heating with **aluminium** ; and J. Percy, by heating with **iron** at a high temp. when all the zinc is volatilized. Zinc oxide has

strongly basic properties, but it is amphoteric, for it unites with other bases—to form salts—**zincates** (*q.v.*)—in which the zinc oxide appears to function as an acid radicle. According to S. Meunier, when cadmium oxide is fused with potassium or sodium hydroxide, double cadmium and alkali oxides are formed. By fusing zinc oxide with eight times its weight of **lead monoxide,** J. Percy obtained a mobile liquid which crystallizes like litharge. According to G. Tammann, zinc oxide immersed in a soln. of **silver nitrate** or sulphate remains white in diffused light, but in sunlight it is rapidly blackened ; and, when the zinc oxide is removed with acetic acid, silver oxide, Ag_2O, remains. The rate of the reaction depends on the physical condition of the oxide. The reaction was studied by V. Kohlschütter and A. d'Almendra. It occurs with other basic oxides, but not with acidic oxides.

H. W. F. Wackenroder [19] showed that ignited zinc oxide does not unite directly with **water** to form the hydroxide. According to A. Dupré and M. Bialas, a litre of water dissolves from 0·0042 to 0·0046 part of zinc oxide at 18°. According to F. Kunschert, soln. of zinc oxide in **alkali hydroxides** have ions ZnO_2'', $HZnO_2'$, and OH', and the difference of potential of zinc against an alkali zincate soln. relative to the normal hydrogen electrode is $1·130–0·029 \log C/[OH]^5$, where C denotes the conc. of the zincate ; and the bracketed symbol, the conc. of the hydroxyl ions in mols per litre. F. Förster and O. Günther found 100 c.c. of a 20 per cent. soln. of sodium hydroxide dissolves in a few hours, calcined zinc oxide eq. to 2·97 grms. of zinc ; precipitated zinc oxide is more rapidly dissolved—*vide* zincates. L. Rolla and R. Salani measured the decomposition tension of mixtures of fused sodium hydroxide and zinc oxide or cadmium oxide. F. Stromeyer found cadmium oxide is readily soluble in aq. ammonia. Calcined zinc oxide is also dissolved by aq. ammonia, but only in the presence of ammonium salts. According to H. Brandhorst, roasted blende is not completely soluble in ammonium carbonate soln., possibly because of the formation of zinc ferrite during the roasting. According to G. Rigg, the solubility of zinc oxide in **ammonium carbonate** soln. reaches a maximum with a definite conc. of carbon dioxide. Expressing the results in kgrms. per 10 litres of soln. with 1·2 kgrms. of NH_3, then with a conc. C of carbon dioxide,

C	0·60	0·65	0·80	0·90	0·95	1·10	1·15	1·30	1·35	1·50
ZnO	1·15	1·37	1·54	1·60	1·73	1·90	1·86	1·74	1·54	1·43

H. Brandhorst obtained a precipitate of ammonium zinc carbonate (*q.v.*) by boiling the soln. These soln. have been studied by H. Wächter, O. Kühling, and C. R. C. Tichborne. The data with cadmium oxide are not consistent. F. Stromeyer said that the precipitate is not soluble in aq. soln. of ammonium carbonate ; J. F. John, and W. Herapath said it is slightly soluble ; and E. D. Clarke said it is very soluble in that menstruum. F. de Lassone found that zinc oxide is dissolved by potash-lye, **lime-water,** and aq. **ammonia.** Zinc oxide is dissolved by a soln. of **ferric chloride** or **ferric sulphate,** and eq. amount of ferric hydroxide is precipitated. According to M. Prud'homme and F. Binder, zinc chromate is produced when zinc hydroxide is treated with **potassium dichromate.** L. Kahlenberg and H. W. Hillger found zinc oxide to be soluble in a boiling soln. of **potassium tartrate.** According to A. Naumann, zinc oxide is insoluble in **acetone.**

Zinc oxide mixed with oil dries to a hard film, basic lead carbonate or white-lead dries to a much softer and more chalk-like surface. Just as zinc added to certain metals gives hardness to the resulting alloy, so, by analogy, zinc oxide added to white-lead produces a pigment which when mixed with oil and applied as a paint gives a harder and more durable surface than the white-lead alone.

P. Drinker [20] has given a review of the bibliography of the toxicity of zinc oxide, and of the conditions under which zinc oxide produces brass-founders' ague are discussed. Ordinary zinc oxide dust as produced, for example, in packing zinc oxide pigments does not produce the ague, whereas that produced by the burning of zinc does. It is suggested that the oxide in the first case has been flocculated

by adsorption of moisture, and is therefore deposited on the walls of the nasal passage or trachea and does not reach the lungs, whereas in the second case the oxide is in a highly dispersed state as a very fine dry powder which readily passes into the lungs, where the particles offer the maximum surface for phagocytosis and ultimate soln. In the second case, zinc is found both in the urine and the fæces, whereas in the first case practically none is found in the urine, showing that very little zinc has been dissolved.

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§ 10. The Hydroxides and Peroxides of Zinc and Cadmium

R. Schindler[1] observed that when zinc in contact with iron is immersed in aq. ammonia, hydrogen is evolved, and in about 8 days, there are deposited on the zinc, and on the sides of the glass vessel, small, transparent, colourless, rhombic prisms of zinc hydroxide, $Zn(OH)_2$. F. F. Runge, A. Cornu, H. Euler and R. de Forcrand prepared the crystals in a similar manner. J. Nicklès also employed the method for crystals of cadmium hydroxide. H. Euler prepared hydroxides, by precipitation from the nitrate, which appeared to have a varying solubility in ammonia. F. Goudriaan found that the precipitate obtained by adding ammonia to a soln. of zinc nitrate or chloride immediately becomes more gritty, heavier, and less gelatinous when washed a few times with boiling water. When dried at 100°, the product contained 0·6 per cent. water. The solubility in sodium hydroxide also decreases when the hydroxide is kept for a longer time. O. Klein distinguished three forms of the hydroxide. If a soln. of zinc sulphate is allowed to drop into one of potassium hydroxide until the white precipitate just fails to redissolve, the soln. is sat. with respect to the modification *A*. In time this soln. deposits a modification *B*, which often forms regular crystals. If collected and dried, *B* passes into a still less soluble modification *C*. The solubility of all three modifications in soln. of different conc. has been determined. *A* has the composition $H_2Zn_2O_3$, *B* and *C* have the composition $Zn(OH)_2$. F. Goudriaan showed that amorphous gelatinous zinc hydroxide is a phase with a varying proportion of water, the proportion of water depends on the mode of preparation, the age, etc. The amorphous product is not stable at 100°, but is rather in a metastable state with a tendency to stabilization to ZnO. The crystalline hydroxide can be obtained as a phase of constant composition :

To 50 c.c. of *N*-KOH add *N*-$ZnSO_4$ from a burette until the hydroxide first formed has redissolved, and a point is reached at which the liquid remains slightly turbid when shaken. When vigorously shaken, or when the glass wall is scratched, and the soln. allowed to stand for a few minutes, a heavy sandy precipitate is formed. Seeding with crystals previously obtained accelerates the crystallization. Under the microscope, the powder consists of small elongated bar-shaped crystals. They filter easily, and, unlike the amorphous product, they can be readily cleaned by washing. The crystals dried at 40°–50° have the composition $Zn(OH)_2$.

A. C. Becquerel obtained crystals of zinc hydroxide by placing a rod of zinc, wound

with copper wire, in a soln. of silicic acid in caustic lye. He assigned the formula $Zn(OH)_2$ to the regular octahedrons so obtained. Colloidal zinc hydroxide is obtained by treating a soln. of zinc nitrate with insufficient potassium hydroxide for complete precipitation, and washing the product; if an excess of the alkali is used, or if a soln. of zinc chloride or sulphate is employed, the product is not nearly so pure. W. Herz, A. Hantzsch, B. B. Kuriloff, and R. Lorenz employed a similar process. They commented on the difficulty in separating the adsorbed alkali hydroxide, and showed that some sulphate is also retained very tenaciously—possibly as basic sulphate. V. T. Hall commented on the adsorption of chlorides by the precipitated hydroxide, and F. Goudriaan showed that the nitrate is likewise adsorbed by the precipitate. C. E. Linebarger showed that the amount of alkali required for the reaction is dependent on the conc. and temp. of the soln. J. Lefort and P. Thibault showed that the presence of gum hinders the precipitation. S. E. Linder and H. Picton prepared the hydroxide as a transparent gelatinous mass. F. Stromeyer likewise prepared cadmium hydroxide by adding potassium hydroxide to a soln. of a cadmium salt; and by treating cadmium oxide with a soln. of potassium hydroxide. W. Bonsdorff recommended precipitating a soln. of cadmium nitrate with sodium hydroxide free from carbon dioxide for cadmium hydroxide; and L. Schaffner used potassium hydroxide as precipitant, and recommended dil. soln. O. Follenius found tartaric acid hinders the precipitation in the cold; sugar hinders it when hot; while citric, malic, succinic, and benzoic acids have no influence. Silver oxide was found by D. Vitali to precipitate partially the cadmium as hydroxide from soln. of cadmium sulphate. W. Vaubel added ammonia to a soln. of zinc salt until it reacted neutral with litmus and reddened with phenolphthalein, and boiled the soln. The presence of ammonium salts hindered the precipitation. A. Vogel and C. Reischauer mixed a soln. of zinc nitrate with an excess of ammonia, and introduced a piece of zinc into the liquid; crystals of the hydroxide were gradually formed and a gas was evolved. F. J. Malaguti, M. Sarzeaud, J. Ville, and A. Cornu prepared crystals of zinc hydroxide more rapidly by the slow electrolysis of an ammoniacal soln. of zinc oxide. The yield is better if finely powdered zinc carbonate be added to the electrolyte. P. Meyer electrolyzed a very dil. soln. of hydrogen peroxide with a zinc anode, and an inert cathode; R. Lorenz electrolyzed an alkali salt with zinc anode, or a cadmium salt with a cadmium anode, and platinum cathodes; O. and H. Strecker electrolyzed soln. of sodium chloride or chlorate with a cadmium anode; and E. Leriche electrolyzed a soln. of sodium chloride with a zinc anode and an iron cathode. M. Malzac treated zinc blende with aq. ammonia, exposed to air.

D. Lance obtained the hydroxides directly from the ores by treatment with aq. ammonia or an amine or a mixture of these. The hydroxides are fractionally precipitated by heat in the order: zinc, cadmium, cobalt, nickel, copper, and silver. According to G. Buchner, crystalline cadmium hydroxide is obtained by heating a soln. of 10 grms. of cadmium iodide in 150 c.c. of water; 360 grms. of potassium hydroxide and 13 grms. of water were then added with continuous stirring at 135° until all the hydroxide had dissolved. After 12 hrs., the soln. was diluted with water, and plates of cadmium hydroxide with a mother-of-pearl lustre were produced. A. de Schulten treated a soln. of a cadmium or zinc salt with an alcoholic soln. of potassium hydroxide and dissolved the precipitate, aided by heat, in an excess of the precipitant; on cooling the soln., hexagonal plates of the hydroxide were produced.

The hydroxides of zinc and cadmium are white. They exist in the colloidal (gelatinous) and crystalline states. Cadmium hydroxide assumes two forms: one prepared by adding sodium hydroxide to soln. of cadmium salts gives rise to the yellow sulphide with sodium sulphide, etc.; and another polymerized one is formed when cadmium soln. are poured into soln. of sodium hydroxide or when they are precipitated hot; this hydroxide produces a red sulphide, with an intermediate dicadmium sulphohydroxide, $Cd_2S(OH)_2$, of a fine red colour, but too

unstable for a pigment. J. Morel found the bipyramidal **crystals** of zinc hydroxide belong to the rhombic system, and have the axial ratios : $a : b : c = 0{\cdot}6048 : 1 : 0{\cdot}5763$. C. Bödeker obtained regular octahedral crystals by allowing a sat. soln. of zinc hydroxide to stand for a week, and these crystals are thought to be the same as those obtained by A. C. Becquerel, by allowing zinc in contact with copper to stand in a soln. of potassium hydroxide. S. Surawicz explained the existence of rhombic and regular octahedral crystals of zinc hydroxide, and hexagonal zinc oxide by assuming the existence of isomeric, metameric, and polymeric forms of zinc oxide in which the water is regarded as water of crystallization. A. de Schulten said that the crystals of cadmium hydroxide belong to the trigonal system. J. Nicklès gave 2·677 for the **specific gravity** of zinc hydroxide, and E. Filhol gave 3·053 ; A. de Schulten gave 4·79 for the sp. gr. of cadmium hydroxide at 15°.

H. Rose [2] found cadmium hydroxide loses its water when heated above 300°. According to R. de Forcrand, colloidal zinc hydroxide obtained by precipitation has not a fixed composition, and at ordinary temp., in the presence of phosphorus pentoxide, it gives off water slowly ; and when heated the loss of water is probably accompanied by polymerization, when the temp. rises above 250°. F. Goudriaan found that crystalline zinc hydroxide is metastable at 30° and slowly passes into the oxide. The hydroxide dehydrated at a low temp. takes up water when exposed to a moist atm. When the precipitated hydroxide, washed in an atm. free from carbon dioxide, is dried on a porous plate over sulphuric acid, and then for 3–4 days over phosphorus pentoxide, it has a composition corresponding with $ZnO : H_2O = 3 : 5$, and its heat of soln. in dil. sulphuric acid is 18·48 Cals. ; when dried for 3–4 weeks, the ratio is 3 : 4, and the heat of soln. is nearly the same as before. When the 3 : 5 hydroxide is heated for 12 hrs. at 160°, the ratio is 4 : 5 at constant weight, and the heat of soln., 18·83 Cals. ; at 250°, the ratio is 5 : 2, and the heat of soln., 23·23 Cals. ; and at a red heat, zinc oxide with a heat of soln. 23·91 Cals. is formed. J. Thomsen gave −2·75 Cals. for the heat of hydration of crystallized zinc hydroxide and liquid water ; or −4·18 Cals. with solid. G. Massol gave +4·32 Cals. ; and R. de Forcrand +2·19 Cals. with water liquid, and 0·76 Cal. with water solid. W. Herz, and A. Hantzsch assumed different modifications are formed during the drying of colloidal zinc hydroxide. J. M. van Bemmelen, and B. Kuriloff have studied the conversion of the colloidal to the crystalline states. The **heats of neutralization** of an eq. of zinc and cadmium hydroxides, $\frac{1}{2}M(OH)_2$, respectively in hydrochloric acid are 9·89 Cals. and 10·145 Cals. (M. Berthelot) ; in hydrofluoric acid, 12·55 and 12·78 Cals. (E. Petersen) ; in hydrocyanic acid, 8·11 and 7·22 Cals. (A. Joannis) ; in nitric acid, 9·858 and 10·16 Cals. (M. Berthelot) ; in one eq. of sulphuric acid, 11·702 and 11·91 Cals. (M. Berthelot) ; and in one eq. of carbonic acid, 5·5 and 6·495 Cals. (M. Berthelot) ; J. Thomsen found for zinc hydroxide $Zn(OH)_2 + H_2SO_4$ aq., 23·41 Cals. ; with 2HCl aq., 19·88 Cals. ; with $2HNO_3$ aq., 19·83 Cals. ; with $2H_2S$ aq., 17·97 Cals. ; and with $2H_2C_2O_4$, 18·03 Cals. For the **heats of formation** of cadmium and zinc hydroxides, J. Thomsen gave $Zn + O + H_2O = Zn(OH)_2 + 82{\cdot}68$ Cals., and $Cd + O + H_2O = Cd(OH)_2 + 65{\cdot}68$ Cals.

E. Goldstein [3] studied the action of cathode rays on the **phosphorescence** of cadmium hydroxide and salts—*vide* cadmium oxide. P. Blackman gave for the **molecular conductivity,** μ, of soln. with a mol of hydroxide in v litres of water :

v .	1000	500	200	100	50	33·3	20
μ .	214	213	210	205	203	98	95

J. K. Wood found that the weaker hydroxyl of zinc hydroxide has a basic dissociation constant of $K = 1{\cdot}45 \times 10^{-9}$. R. Lorenz found the difference of **potential** of zinc hydroxide with respect to the normal hydrogen electrode, in neutral soln., to be −0·31 volt ; and C. Immerwahr, of cadmium hydroxide against 0·05*N*-NaOH with respect to the calomel electrode 0·750 volt at the beginning and 0·855 volt at the end. S. Meyer found the **magnetic susceptibility** of powdered zinc hydroxide (vacuum=0) is $-0{\cdot}42 \times 10^{-6}$ mass units at 18°.

The **solubility** of zinc hydroxide in **water** was found by W. Herz [4] to be $2{\cdot}6\times10^{-6}$ grm. per litre, and for cadmium hydroxide, he found $2{\cdot}6\times10^{-4}$. S. Labendzinsky, and G. Bodländer also made measurements of this constant. Zinc and cadmium hydroxides are amphoteric in that they act both as acids and as bases. According to G. Carrara and G. B. Vespignani, the basic energy of the metallic hydroxides corresponds with their position in the periodic table, for they fall in the order of decreasing strength : Mg, Cu, Zn, Cd, Al, Fe. H. W. F. Wackenroder found that when zinc oxide is boiled with an aq. soln. of **sodium or potassium carbonate,** some alkali is adsorbed, and the oxide exhibits an alkaline reaction ; the alkali can be removed by a prolonged washing with water. According to A. Colson, when a soln. of **sodium sulphate** is added to zinc oxide (neutral to phenolphthalein) suspended in water, the mixture becomes increasingly alkaline, owing to the liberation of sodium hydroxide, and the formation of what he regarded as a basic sulphate, $(Zn.O.ZnOH)_2SO_4$. W. Bersch found that freshly precipitated cadmium hydroxide dissolves in aq. soln. of **potassium and sodium halides or thiocyanates** liberating the alkali hydroxide ; the calculated heats of reaction are all negative and with KCl is —818 cals. ; with NaCl, —754 cals. ; KBr, —738 cals. ; NaBr, —744 cals. ; KI, —716 cals. ; and NaI, —716 cals. W. Biltz and F. Zimmermann found that when well-washed zinc or cadmium hydroxide is treated with $\frac{1}{10}N$-**silver nitrate,** the hydroxide is discoloured owing to the formation of silver oxide ; and $\frac{1}{10}N$-**mercuric nitrate** produces a yellowish-red discoloration for an analogous reason. H. N. Stokes found that **ferrous sulphide** does not react with zinc hydroxide in the cold or at 100°, but at 160° ferrous hydroxide and zinc sulphide are slowly formed. According to G. Lunge and H. Landolt, if **chlorine** be passed into water in which zinc hydroxide is suspended, zinc hypochlorite and chlorate are formed in quantities which increase as the temp. rises. R. von Wagner found zinc hydroxide is slowly converted into zinc sulphide by the action of **hydrogen sulphide.** R. Fink investigated the behaviour of zinc hydroxide towards soln. of metallic salts.

F. J. Malaguti,[5] and A. Müller observed that rhombic crystals containing zinc oxide and ammonia are formed on the painted brick-work of a privy. T. Weyl noted that zinc oxide absorbs ammonia gas at a low temp., forming **zinc diammino-oxide,** $ZnO(NH_3)_2$. Zinc hydroxide was found by E. Firnhaber to be readily dissolved by aq. **ammonia,** while the ignited oxide does not dissolve at all ; but, according to R. Schindler, the ignited oxide is sparingly soluble in that menstruum, and its solubility is augmented by the presence of traces of ammonium and potassium salts—the phosphates were found to be most favourable, then follow arsenates, chlorides, sulphates, nitrates, acetates, carbonates, tartrates, citrates, and sulphites ; succinates and benzoates are favourable only in dil. soln. ; borates, iodides, chlorates, arsenites, oxalates, and gallates unite with the zinc oxide. F. F. Runge found that zinc in contact with iron dissolves slowly in aq. ammonia with the evolution of hydrogen and the formation of a colourless soln. The zinc dissolves in the absence of iron, but more slowly. A soln. can be obtained containing 3·95 parts of zinc oxide, and 7·68 parts of ammonia per 100 parts of soln. The conc. soln. becomes turbid when diluted with over 15 times its vol. of water. According to G. C. Wittstein, and A. Bonnet, when the soln. is evaporated in air, it furnishes needle-like crystals containing carbonates of zinc and ammonium, and when evaporated on a sand-bath, it gives an odourless mass, which is soluble in water, and which gives off ammonia when treated with potassium hydroxide. J. J. Berzelius found that lime-water, strontia-water, or baryta-water precipitates from the ammoniacal soln. a compound (or mixture) of zinc oxide with the earthy base. A. M. Comey and C. L. Jackson could not prepare ammonium zincate.

D. P. Konowaloff found that the vap. press., p, of ammonia in aq. soln. is depressed in the presence of dissolved salt such that if p_1 represents the press. of the dissolved salt and n and m the number of mols of ammonia and salt respectively in a litre of soln., then $p_1=p(n-km)$, where k is a constant whose value is 4 for

cadmium and zinc nitrates. This is taken to mean that each atom of zinc or cadmium is probably united with 4 mols of ammonia—say, **zinc tetrammino-oxide,** $Zn(NH_3)_4O$. From solubility determinations and measurements of the e.m.f. of conc. cells, H. Euler also deduced that the complex cation in ammoniacal soln. of zinc salts is $Zn(NH_4)_2$, and W. Bonsdorff measured the electrical conductivity of soln. of zinc or cadmium hydroxide in aqua ammonia. According to W. Bonsdorff, the solubility of zinc hydroxide in aq. ammonia at 25° is

Normality of NH_3 .	0·321	0·643	1·215	1·928	2·570	3·213
ZnO, grms. per litre	0·34	0·845	2·70	5 07	7·01	10·16

H. Euler, and W. Bonsdorff also inferred from measurements of the transport numbers that a measurable amount of *ammonium zincate* is not present in ammoniacal soln. of zinc oxide. W. Herz found that zinc is present in the diffusate from ammoniacal soln. of zinc hydroxide. B. B. Kuriloff found that the excess of ammonia necessary to dissolve the precipitate formed when ammonia is added to a soln. of zinc chloride or sulphate is greater the more dil. the soln. W. Herz studied the equilibrium represented by the scheme $Zn(OH)_2+2NH_4Cl \rightleftharpoons ZnCl_2+2NH_4OH$; similarly also with soln. of zinc sulphate and nitrate, and with cadmium salts. W. Herz found that the solubility of zinc oxide is less with the mono-substituted ammonias, and this the more the higher the mol. wt. of the amine; zinc oxide is not soluble in the disubstituted ammonias. A. Bonnet found plant fibres absorb zinc oxide from an ammoniacal soln. when treated with an alkali, and it is not removed by washing. A. Windaus studied the action of an ammoniacal soln. of zinc oxide on sugars; and K. Inouje, on *d*-galactose and *d*-arabinose.

F. Stromeyer found that when cadmium oxide is treated with aq. ammonia, its colour first becomes white, and it then dissolves; the soln. on evaporation forms the gelatinous hydroxide; while H. W. F. Wackenroder noted that potassium hydroxide precipitates cadmium hydroxide from the ammoniacal soln. of the oxide. The solubility of cadmium hydroxide in aq. ammonia has been measured by H. Euler, and W. Bonsdorff; the latter found at 25°:

Normality of NH_3 .	0·5	1·0	1·8	4·6
CdO . . .	0·24	0·62	1·33	4·92 grms. per litre

From the solubility of the oxide in aq. ammonia, and the conductivity and potential of the soln., W. Bonsdorff showed that the ammoniacal soln. probably contains complexes of cadmium tetrammino-oxide, $Cd(NH_3)_4O$; and H. Euler found the equilibrium constant to be $k=1{\cdot}0\times10^{-7}$. The complexes were studied by W. Gaus, H. M. Dawson and J. McCrae, W. Bonsdorff, etc. E. Ebler compared the tendency of the different metals to form complexes with ammonia. W. Bonsdorff found that the ammonia-base formed by cadmium oxide is rather weaker than the one formed with nickel oxide, and he found that the stability of the complex with zinc is about 100 times greater than that of the complex with cadmium.

The peptization of zinc hydroxide by a soln. of sodium hydroxide in glycerol or sugar is a case of chemical action because the electrical conductivity of the alkali soln. is lowered by the addition of the zinc hydroxide—*vide* mercuric hydroxide. As previously indicated, zinc dissolves slowly in a soln. of **potassium or sodium hydroxide,** forming what is regarded as a soln. of alkali zincate. The ignited oxide dissolves slowly, and the hydrated oxide rapidly in the alkali lye. According to G. Bonnet,[6] two parts of zinc oxide dissolve in five parts of potash lye of sp. gr. 1·3; and W. J. Sharwood noted that the solubility of zinc oxide is less with soln. of potassium hydroxide than with soln. of sodium hydroxide, and that with dil., say $\frac{1}{10}N$-, soln. of the alkali-lye—thus cold soln. with 100 mols of potassium hydroxide or sodium hydroxide dissolved respectively 2·4 and 4·5 mols of zinc oxide; hot soln. dissolve rather more, but when boiled, the soln. is decomposed and zinc oxide is precipitated. Dil. soln. of alkali-lye are readily decomposed; and conc. soln.

become turbid when diluted with a large proportion of water. A. B. Prescott found that more than four mols of KOH are needed for the soln. of one mol of $Zn(OH)_2$, and zinc hydroxide is precipitated when the sat. soln. is diluted with 12 vols. of water. About three times as much alkali is needed for the soln. of the zinc hydroxide at 50° as at 16°–17°. According to W. Herz, freshly precipitated zinc hydroxide readily dissolves in excess of potassium hydroxide and is completely dissolved when for 1 Zn there are 6 OH groups. If, however, the zinc hydroxide is previously dried at 60°–70° in a vacuum desiccator, it becomes comparatively difficult to dissolve, and is only completely dissolved when for 1 Zn there are 35·8 OH groups in the soln. B. Kuriloff found that when potassium hydroxide is added to a soln. of zinc chloride or sulphate, the excess needed to dissolve the precipitate first formed is greater the more dil. the soln., and greater for the sulphate than for the chloride. J. K. Wood found that the solubility of zinc hydroxide in soln. of sodium hydroxide at 25° is :

Mols NaOH . .	0·2636	0·3871	0·5414	0·9280
Mols $Zn(OH)_2$ . .	0·00311	0·0057	0·0129	0·0425

J. Rubenbauer found that the quantity of zinc hydroxide dissolved by soln. of sodium hydroxide varies with the conc. of the latter. There is a maximum solubility for the atomic ratio : Zn : Na=1 : 3. The maximum is attributed to the decreased solubility owing to increasing hydrolysis the more dil. the soln., and to the dehydration of the hydroxide by the conc. alkali soln. whereby it is transformed into a less soluble form. When zinc hydroxide is treated with alkali, more dissolves at first than corresponds with the true equilibrium under the prevailing conditions, for such soln. spontaneously deposit more or less zinc hydroxide according to the conc. When potassium hydroxide is gradually added to a soln. of zinc sulphate, zinc hydroxide is precipitated, and subsequently redissolved. Fig. 25 shows the relation between the amount of zinc hydroxide precipitated and the proportion of potassium hydroxide in soln. The precipitation of zinc hydroxide is complete when 1·62 mols of potassium hydroxide per mol of zinc sulphate are present in the soln., and soln. is complete only when 13·2 mols of potassium hydroxide per mol of zinc sulphate are present.

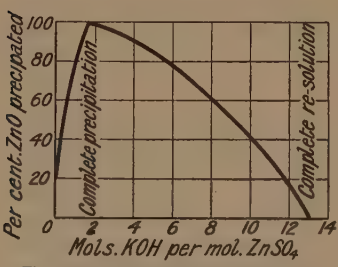

Fig. 25.—The Precipitation of Zinc Hydroxide by Potassium Hydroxide.

According to A. Hantzsch, zinc hydroxide separates from its alkaline soln. as a fine, dense powder soluble with difficulty in sodium hydroxide soln., but he does not believe an isomeric or polymeric modification is formed, rather is the diminished solubility to be attributed to (i) a physical alteration of the surface, and (ii) to a dehydration of the hydroxide by the alkali. A. W. Buchner, and R. Schindler noted that when the soln. of zinc hydroxide in potassium hydroxide is exposed to air, a precipitate containing zinc oxide, potassium hydroxide, and carbon dioxide is formed ; if the soln. be boiled, zinc hydroxide alone is precipitated. If some silica is present, a double silicate of zinc and potassium is precipitated.

R. Kremann found that when an alkaline soln. of zinc hydroxide is electrolyzed, the proportion of zinc at the anode increases, and the anion is in consequence assumed to contain zinc, and the soln. is not to be regarded as a colloidal soln. of zinc hydroxide. G. Bredig, however, objected that the migration experiments do not prove that anionic complexes are present because colloidal suspensions themselves migrate under the influence of an electric current ; but R. Kremann replied that the order of magnitude of the migration of zinc in alkaline soln. shows that the phenomenon is not due to migration in colloidal soln. W. Biltz found that during electrolysis colloidal zinc and cadmium hydroxides migrate to the cathode.

W. Herz found that when a soln. of zinc hydroxide in alkali lye is dialyzed, very little passes through the membrane, but hydroxide is precipitated on the membrane, and he therefore inferred that the alkali soln. contains part of the zinc as zincate, and part as colloidal oxide. F. G. Cottrell also studied the rate of diffusion of these soln. When an alkaline soln. of zinc hydroxide is warmed or when sodium chloride is added, most of the zinc hydroxide separates out, and from the electrical conductivity, and the effect on the speed of hydrolysis of ethyl acetate, A. Hantzsch inferred that the zinc hydroxide is an extremely weak acid, and is mainly present in soln. in the colloidal form; that the hydroxide acts as a monobasic acid; and that there are no grounds for assuming the existence of a dibasic acid, H_2ZnO_2. A. Hantzsch said:

> Zinc and beryllium hydroxides behave like very weak acids, but the former scarcely deserves the name acid because the existence of alkali zincates in aq. soln. can no longer be established for zinc hydroxide spontaneously separated from the soln. (almost the whole of it under certain conditions) when flocculated by warming or by treatment with sodium chloride, as in the case of colloidal soln. The main quantity of zinc hydroxide in these soln. is therefore present in the colloidal form.

O. Klein suggested that A. Hantzsch was misled by using very dil. soln., for the solubility of the oxide is proportional to the amount of alkali present, and this agrees with the assumption that a definite compound is formed. As previously indicated, O. Klein assumed that there are three modifications of the hydroxide —*vide* beryllium hydroxide. By dropping a soln. of zinc sulphate into a soln. of potassium hydroxide until the precipitate just fails to dissolve, it is assumed that the soln. is just sat. with the most soluble and least stable *A*-form; if the soln. be allowed to stand it deposits crystals of the *B*-form; and these soon pass into the least soluble *C*-form. Expressing conc. in mols per litre, at 18°,

	A-form			*B*-form			*C*-form		
Conc. KOH . .	0·540	0·330	0·100	0·310	0·200	0·06	0·280	0·190	0·0031
Conc. $Zn(OH)_2$.	2·78	2·02	0·90	2·76	2·00	0·94	6·25	0·323	0·26

The whole of the results are represented by the graphs, Fig. 26. It is assumed that the *A*-form is $H_2Zn_2O_3$, which ionizes $H_2Zn_2O_3 = 2H^{\cdot} + Zn_2O_3''$, so that $[H^{\cdot}]^2(Zn_2O_3'') = k_1 = 0{\cdot}68 \times 10^{-29}$. The *B*-form is assumed to be H_2ZnO_2, which ionizes $H_2ZnO_2 \rightleftharpoons 2H^{\cdot} + ZnO_2''$, so that $[H^{\cdot}]^2[ZnO_2''] = k_2 = 0{\cdot}71 \times 10^{-29}$. The *C*-form is similar in composition to the *B*-form, and its constant $k_3 = 0{\cdot}27 \times 10^{-29}$. These assumptions agree with the observations of W. Herz, J. K. Wood, and J. Rubenbauer. O. Klein added that there is no evidence of colloidal zinc hydroxide in the soln.

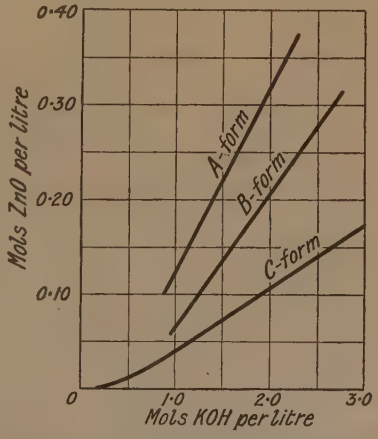

Fig. 26.—Solubility of the Different Forms of Zinc Hydroxide in Solutions of Potassium Hydroxide, at 18°.

G. Carrara and G. B. Vespignani measured the electrical conductivity of soln. of 0·03575 grm. of zinc oxide in 100 c.c. of $\frac{1}{5}N$-KOH, when the soln. is so diluted that it contains an eq. of KOH in v litres, and found:

v . .	5	10	20	40	80	160	320	640
λ . .	200·23	202·10	212·98	215·48	215·44	213·92	207·36	190·72

From electrometric measurements F. Kunschert inferred that a soln. of zinc hydroxide in conc. sodium hydroxide contains sodium zincate, Na_2ZnO_2, *i.e.* the sodium salt of dibasic zincic acid, H_2ZnO_2, which furnishes bivalent anions ZnO_2'';

with dil soln. of the alkali hydroxide sodium hydrozincate, $NaHZnO_2$, is present, and it furnishes univalent ions $HZnO_2'$. Both salts are stable only in the presence of an excess of alkali. G. Bodländer calculated the stability constant and the energy of formation of $HZnO_2$, and obtained respectively $1{\cdot}9\times10^6$ and 8340 $+670 \log [Zn][OH]^3/C$ cals., where C denotes the conc. of the complex ion in mols per litre; F. Kunschert obtained respectively $2{\cdot}5\times10^6$ and 16,520 cals. at 18°. G. Bodländer also found the e.m.f. of the soln. of sodium zincate in contact with the metal against the hydrogen electrode, to be $1{\cdot}130-0{\cdot}029 \log C/[OH]^3$; and for the heat of formation in cals. per gram-ion of the complex from the metal and anions, he obtained $52600-1340 \log C/[OH]^3$. J. K. Wood found 60 per cent. hydrolysis in a $\frac{1}{10}N$-soln. of sodium zincate.

J. Moir regards the dissolution of zinc hydroxide by a soln. of an alkali hydroxide as an equilibrium phenomenon between the alkali and zincic acid. The equilibrium may be reached from both sides: (i) adding an excess of zinc hydroxide to an alkali lye; or (ii) diluting a conc. soln. sat with zinc hydroxide. J. Moir found no evidence of the existence of a definite compound in his solubility curves of zinc hydroxide in soln. of $0{\cdot}01N$- to $7N$-alkali. If x represents the number of mols of potassium or sodium hydroxide, and y the number of mols of zinc oxide dissolved, J. Moir found the observed results could be approximately represented by the empirical relation: $y(x+2)=0{\cdot}004x(79x+6)$. The observed results obtained by diluting a sat. soln. are sometimes abnormal owing to the persistence of a state of supersaturation, but in time, a state of stable equilibrium is attained. P. Schoop has studied the electrochemical formation of alkali zincate soln.

A. Bonnet found that when a soln. of potassium zincate is evaporated to dryness, and the residue fused, an enamel-like mass is formed from which water extracts the alkali, and when the soln. is treated with eight vols. of alcohol, nearly all the zinc oxide is deposited. F. Wöhler obtained a basic zinc carbonate by exposing in air a soln. of zinc oxide in one of sodium hydroxide. M. Laux found that when a conc. soln. of potassium zincate is covered with a layer of alcohol, small shining crystals of **potassium zincate,** K_2ZnO_2, containing $ZnO : K_2O=1:1$, are deposited; the crystals are readily decomposed by water, and when the soln. is boiled, a white powder is formed containing $ZnO : K_2O=2:1$. A. L. Voege obtained this compound in a secondary reaction between electrolytically formed potassium hydroxide and a zinc cathode; G. Carrara and G. B. Vespignani obtained it by the dissolution of zinc oxide in an excess of a moderately conc. soln. of potassium hydroxide; and W. J. Sharwood by the soln. of zinc cyanide in a dil. soln. containing two or more than two mols of potassium hydroxide. E. Frémy reported that when alcohol is added to a conc. soln. of potassium zincate, long needles of *potassium dizincate*, $K_2Zn_2O_3$, with $ZnO : K_2O=2:1$, are deposited; these are immediately decomposed by water, forming zinc and potassium hydroxides. A. M. Comey and C. L. Jackson did not confirm the existence of this compound, but obtained instead amorphous zinc oxide. W. J. Sharwood claimed to have made a compound, $K_2ZnO_2.8KOH$, by the action of potassium cyanide on zinc oxide. J. Moir found no grounds for assuming the existence of these products as chemical individuals.

A. M. Comey and C. L. Jackson found that when alcohol is shaken with a conc. soln. of zinc oxide in sodium hydroxide, the liquid separates into two layers. The lower aq. layer was treated with alcohol two or three times when it solidified to a crystalline mass which melts at about 70°, and has the composition $Na_4H_2Zn_3O_6.17H_2O$. The alcoholic soln. deposits lustrous needles which do not melt at 300°, and have the composition $2(NaO.ZnOH).7H_2O$, and correspond with E. Frémy's potassium compound. F. Förster and O. Günther could prepare only one **sodium zincate,** $NaO.Zn.OH.3H_2O$, in white needles with a silky lustre by crystallization from a soln. of zinc in sodium hydroxide. E. Jordis obtained crystals of sodium zincate, $Zn(ONa)_2.nH_2O$, in a galvanic cell in which zinc was employed as a negative pole in a soln. of sodium hydroxide. F. Goudriaan found only one stable sodium zincate, $Na_2ZnO_2.4H_2O$, at 30°, and the conditions of

equilibrium are indicated in Table III, and Fig. 27. Sodium zincate forms what is called an *incongruent solution*, for, on adding water, it does not yield a

TABLE III.—SYSTEM Na_2O—ZnO—H_2O AT 30°.

Percentage composition of solution.			Solid phases.
Na_2O	ZnO	H_2O	
11·8	2·6	85·6	ZnO
24·6	12·6	62·8	ZnO
27·3	16·0	56·7	ZnO
27·8	16·5	55·7	ZnO+$Na_2O.ZnO.4H_2O$
28·0	14·9	57·1	$Na_2O.ZnO.4H_2O$
33·2	11·2	55·6	$Na_2O.ZnO.4H_2O$
36·8	9·9	51·6	$Na_2O.ZnO.4H_2O$
39·2	9·7	51·1	$Na_2O.ZnO.4H_2O$+$Na_2O.3H_2O$
39·4	9·0	51·6	$Na_2O.3H_2O$
40·7	2·0	57·3	$Na_2O.3H_2O$
40·9	1·1	58·0	$Na_2O.3H_2O$
41·9	0·0	58·1	$Na_2O.3H_2O$

simple soln., but one of the components separates out. Not only does the addition of water to the solid salt cause a separation of zinc oxide, but the dilution of the soln. of sodium hydroxide produces the same result. The range of stability is indicated in Table III and in the accompanying diagram. The salt is decomposed by soln. below a conc. of one part of sodium hydroxide to two parts of water. The crystals are also hydrolyzed by 96 per cent. alcohol, and a mixture of amorphous zinc oxide or hydroxide and sodium zincate is formed, the relative proportions of the two depend on the proportion of alcohol employed and the duration of the operation. These facts also explain the various results obtained by different investigators, and show that many mixtures must have been reported as chemical individuals. F. Goudriaan studied the conditions of equilibrium of the ternary system: Na_2O—ZnO—H_2O at 30°; and a few data from his list are indicated in Table III. The results are plotted in Fig. 27, where the curve *AB* represents the increasing solubility of zinc oxide in soln. of increasing conc. in sodium hydroxide; *BC*, the solubility with $Na_2O.ZnO.4H_2O$ as solid phase; and *CD*, the solubility with $Na_2O.3H_2O$, *i.e.* $NaOH.H_2O$, as solid phase. *AF* represents the metastable solubility-curve of crystalline zinc hydroxide, so that other circumstances being equal, the solubility of crystalline zinc hydroxide is greater than that of zinc oxide. Consequently, at 30° there is only one stable sodium zincate, namely, $Na_2ZnO_2.4H_2O$. All the other zincates which have been reported must be regarded as metastable or as non-existent.

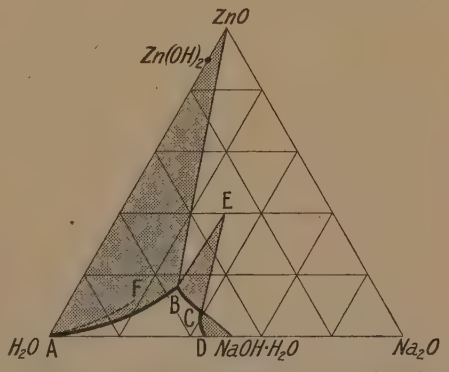

FIG. 27.—Ternary System: ZnO—Na_2O—H_2O at 30°.

According to C. U. Shepard, the mineral *calciozincite* from Franklin, New Jersey, has the composition CaO, 7·56; ZnO, 81·00; H_2O, 4·26 per cent.; its sp. gr. is 3·95. M. Reiche obtained a cement which was very hard, and resistant towards salt soln., by heating a mixture of a mol of zinc oxide with two mols of calcium oxide in the presence of water, and under a high press. G. Bertrand prepared

calcium zincate, $CaH_2(ZnO_2)_2.4H_2O$, or $Ca(O.ZnOH)_2.4H_2O$, in brilliant lozenge-shaped plates when ammonia is withdrawn from the sat. ammoniacal soln. of zinc oxide and lime water, by evaporation over sulphuric acid. The salt absorbs carbon dioxide from air when it becomes opaque, and is decomposed by water into zinc oxide and lime; it does not lose water at 125°, but is decomposed at a dull red heat. The corresponding **strontium zincate,** $SrH_2(ZnO_2)_2.7H_2O$, was made in a similar manner in the form of flattened lozenge-shaped crystals; and **barium zincate**, $BaH_2(ZnO_2)_2.7H_2O$, crystallized in brilliant flattened needles.

According to S. Meunier,[7] cadmium oxide dissolves in molten potassium hydroxide, and, after washing the potassium hydroxide away from the cold mass, yellow crystals of **potassium cadmiate** remain; they contain cadmium oxide, potassium hydroxide, and water. They are insoluble in water, but are slowly decomposed when in contact with that menstruum. Similar results were obtained with sodium hydroxide—**sodium cadmiate.** L. Rolla and R. Salani found that fused sodium hydroxide shows two points of cathodic decomposition, the lower one, 1·20 volts, corresponding with the discharge potential of the hydrogen-ions; the higher point, corresponding with the discharge potential of the sodium-ions, has the value 2·08 volts at 460°, 2·13 volts at 412°, and 2·24 at 364°. With the mixtures containing zinc or cadmium oxide, the decomposition occurring is that of zinc or cadmium hydroxide, the decomposition tensions for the zinc- and cadmium-ions being, respectively, 1·80 and 0·89 volts. When zinc oxide is fused with **magnesium chloride,** K. A. Hofmann and K. Höschele found volatile zinc chloride is formed.

Zinc and cadmium peroxides.—L. J. Thénard [8] obtained *deutoxide de zinc* or zinc peroxide by treating zinc hydroxide with hydrogen peroxide at 0°. The gelatinous mass gives off oxygen slowly at ordinary temp., and rapidly at 100°. When treated with acids, it forms a zinc salt and hydrogen peroxide. L. J. Thénard found that the additional oxygen taken up was rather more than half that originally present in the monoxide, and concluded that per-oxidation was incomplete. R. Haas confirmed these results, and he found the composition of the product varied between Zn_5O_8 and Zn_3O_5, and he considered the presence of hydroxide is necessary for the formation of the peroxide. His product was a white, odourless, tasteless, neutral, gelatinous mass; fairly stable to acids, water, and heat. When a soln. of zinc sulphate is added to an excess of a soln. of sodium hydroxide containing hydrogen peroxide, zinc is precipitated in a peroxidized form. R. de Forcrand obtained a number of intermediate peroxides. For example, $4ZnO.H_2O.3H_2O_2$, or, less probably, $Zn_4O_7.4H_2O$, is obtained by shaking zinc hydroxide suspended in water with hydrogen peroxide containing 2 to 3 times as much active oxygen as is needed to convert the zinc oxide into the dioxide, ZnO_2. The product loses no oxygen in a desiccator at ordinary temp. When heated to 100°, it produces **zinc hydroperoxide,** $3ZnO.H_2O.2H_2O_2$, or, less probably, $Zn_3O_5.3H_2O$ At 190°, it decomposes explosively into hydrated zinc oxide. When $4ZnO.H_2O.3H_2O_2$ is treated with an excess of hydrogen peroxide, it forms $ZnO.H_2O.H_2O_2$, less probably formulated $ZnO_2.2H_2O$. This compound produces $3ZnO.2H_2O_2$, which is less probably represented by $Zn_3O_5.2H_2O$. B. B. Kuriloff claimed that only one definite peroxide, $ZnO_2.Zn(OH)_2$, has been proved to exist, and he regards this as the end-product of the oxidation. J. F. Eijkman boiled a soln. of zinc sulphate, which had been treated with enough aq. ammonia to dissolve the precipitate first formed, with 30 per cent. hydrogen peroxide. The pale-yellow granular precipitate is stable up to nearly 130°. It is soluble in aq. sodium hydroxide with the evolution of oxygen; it explodes when heated to about 212°; and when mixed with aluminium or zinc powder, it burns with a dazzling light. F. W. Sjöström left ignited zinc oxide for several hours in contact with the calculated amount of a 30 per cent. soln. of hydrogen peroxide at —10°. The product was a pasty mass above 2°, and when dried at 35°–40° on a porous plate over soda-lime, it furnished a white powder corresponding with $HO.Zn_2O.O.OH$.

It is not clear whether the product of the action of hydrogen peroxide on zinc oxide is to be regarded as a salt of hydrogen peroxide, or as an addition product with hydrogen peroxide of crystallization. The above-mentioned products can be regarded as mixtures of zinc peroxide with the unconverted hydroxide. O. Carrasco digested zinc oxide with an ethereal soln. of hydrogen peroxide in excess and obtained a product which, when dried at 60°–70°, had the composition $Zn_4O_7.2H_2O$. It is stable at 70°–80°, and is not affected by cold water, but with hot water at 100°, it forms $Zn_3O_5.H_2O$. Both compounds are reddish-yellow powders which explode near 212°. O. Carrasco claimed that these two products are hydrated peroxides, and not additive compounds of condensed hydrates of zinc oxide with hydrogen peroxide, because they contain less water mols. than active oxygen atoms. In structure they differ from the peroxides of other metals, and are to be considered as *perzincic acids* of the following probable constitutions: HO.Zn.O.O.Zn.O.O.Zn.O.O.Zn.OH and HO.Zn.O.O.Zn.O.O.Zn.OH. According to P. Kazanecky, the action of a 30 per cent. soln. of hydrogen peroxide soln. on potassium, sodium, or ammonium zincoxide results in the formation of a white, microcrystalline precipitate, which is found to consist of a zinc peroxide, $ZnO_2.H_2O$, containing an admixture of zinc carbonate, the presence of the latter being due to the strong alkalinity of the soln. in which the reaction takes place. When the peroxide is heated, explosive evolution of oxygen and water occurs at 178°. When heated with dil. sulphuric acid, it yields hydrogen peroxide, whilst, with conc. hydrochloric acid, chlorine is evolved. The peroxide must, indeed, be regarded as consisting of three molecules of ZnO_2, one of which is the dioxide corresponding with an acid anhydride, the other two representing true zinc peroxide:

$$Zn<\begin{matrix}O\\O\end{matrix}(Zn:O:O)_2 3H_2O.$$

P. Kazanecky, and F. W. Sjöstrom are agreed that those zinc peroxides which have been described previously by various authors consist of mixtures derived either from zinc hydroxide, $Zn(OH)_2$, or from zinc hydroperoxide, HO.Zn.O.Zn.OH, and the representatives are respectively HO.Zn.O.OH, or HO.Zn.O.Zn.O.OH. E. Ebler and R. L. Krause proposed the term *peroxydate* for additive compounds of hydrogen peroxide, and *peroxite* for the salts of hydrogen peroxide regarded as a dibasic acid. A soln. of hydrogen peroxide is extracted with ether, and the extract is dried with anhydrous sodium sulphate and added gradually to a cooled soln. of zinc ethyl in dry ether. Ethane is evolved, and a white, amorphous precipitate is formed, which is washed with ether and dried in a vacuum. It has the composition ZnO_2, $\frac{1}{2}H_2O$, is slowly decomposed by acids, yielding hydrogen peroxide, or violently by heat, evolving oxygen. Water hydrolyzes it very slowly, an equilibrium being reached. The compound acts on a photographic plate.

Zinc peroxides have been recommended in various forms as antiseptics because they are odourless, and non-irritant. There are various preparations. E. Merck's *zinc perhydrol* is made by treating dry zinc oxide with pure hydrogen peroxide; F. J. Homeyer's preparation was made by treating sodium or barium peroxide with zinc chloride; M. Frenkel's *ectogan* contains 20 to 60 per cent. of zinc peroxide; R. Wolfenstein precipitated zinc peroxide on alumina; and F. Hinz's preparation was made by the electrolysis of zinc chloride with hydrogen peroxide about the cathode. R. von Foregger and H. Philipp found commercial zinc peroxide averaged 50 per cent. ZnO_2, along with zinc hydroxide and moisture. It is a yellowish-white powder of sp. gr. 1·571; it is very stable, and does not lose its available oxygen at 170°. At 100°, the moisture evaporates without affecting the product itself, so that by this procedure the substance gains in percentage of peroxide. Zinc peroxide suspended in water is very permanent and very slightly soluble (one part in 45,500). In acids of any kind it is readily soluble. Organic matter, if moist, or if acid in reaction, decomposes it gradually. It is indifferent to mineral hydrocarbons, inasmuch as they contain no free acid. This characteristic is essential for the preparation of ointments, a form in which it is widely used.

R. Haas made cadmium peroxide, analogous to zinc peroxide, with a composition ranging from Cd_5O_8 to Cd_3O_5. G. Krüss believed that pure cadmium peroxide could be made by the action of hydrogen peroxide on cadmium hydroxide. B. B. Kuriloff made what approximated to $CdO_2.Cd(OH)_2$, by repeatedly evaporating to dryness a mixture of cadmium hydroxide and a dil. soln. of hydrogen peroxide. The yellow crystalline powder is insoluble in aq. ammonia; it yields hydrogen peroxide when treated with acids; and it is decomposed at 180°. J. F. Eijkman obtained what he regarded as $4CdO_2.Cd(OH)_2$, by boiling an ammoniacal soln. of cadmium hydroxide with hydrogen peroxide. The yellow powder is darkened by exposure to light, and superficially forms cadmium oxide; it explodes at 190°; and is not dissolved by a soln. of sodium hydroxide. W. Manchot reported that cadmium oxide formed by the low temp. oxidation of the metal in air, contains some dioxide, CdO_2.

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§ 11. Zinc and Cadmium Fluorides

H. Moissan found [1] that fluorine has very little action on zinc in the cold, but when heated, the zinc burns with a brilliant light, forming zinc fluoride, ZnF_2. J. L. Gay Lussac and L. J. Thénard obtained a gelatinous precipitate by adding potassium fluoride to a soln. of zinc sulphate, and the precipitate when dried formed white powder ; a similar product was obtained by the action of hydrofluoric acid on zinc. J. J. Berzelius likewise made **cadmium fluoride,** CdF_2, by the evaporation of a soln. of cadmium in hydrofluoric acid. W. Mills prepared fluoride of the metals whose salts are precipitable by ammonia—*e.g.* aluminium, chromium, magnesium, manganese, zinc, etc.—by adding ammonium fluoride, or ammonia and hydrofluoric acid, to a soln. of the chloride or sulphate of the metal. On evaporating soln. of zinc fluoride in dil. hydrofluoric acid, small white rhombic crystals of **tetrahydrated zinc fluoride,** $ZnF_2.4H_2O$, are obtained. J. C. G. de Marignac made anhydrous **zinc fluoride,** ZnF_2, by heating the hydrated salt to 100° ; H. Moissan, by washing the product of the action of hydrofluoric acid on zinc carbonate and drying at 200° ; C. Poulenc, by the action of hydrogen fluoride on zinc or zinc oxide at a red heat, or on hydrated zinc chloride at 800°–900° ; G. Gallo [2] made anhydrous zinc fluoride by heating the hydrated fluoride, or zinc fluosilicate for 2 hrs. at 125° ; C. Poulenc made crystals of anhydrous cadmium fluoride, CdF_2, by the same process as he employed for the zinc salt.

Anhydrous zinc fluoride forms colourless needle-like crystals belonging either to the monoclinic or triclinic system. The crystals of tetrahydrated zinc fluoride belong to the rhombic system with axial ratios, according to J. C. G. de Marignac, $a : b : c = 0{\cdot}6054 : 1 : 0{\cdot}4396$. The sp. gr. of anhydrous zinc fluoride is 4·84 (15°), according to C. Poulenc, and, according to F. W. Clarke, 4·612 (12°) and 4·556 (17°) ;

for anhydrous cadmium fluoride, C. Poulenc gives 6·64 (15°), and F. W. Clarke, 5·994 (22°). W. Biltz said that, assuming the sp. gr. of zinc and cadmium fluorides are 4·84 and 5·994, the respective mol. vol. are 21·4 and 26·09 G. Gallo gave 734° for the m.p. of zinc fluoride. The m.p. of cadmium fluoride, according to T. Carnelley, is 520°, but, according to O. Ruff and W. Plato, it is over 1000°; the best representative values for the m.p. of zinc and cadmium fluorides are respectively 734° and 520°. Zinc fluoride is perceptibly volatile at 800°, but cadmium fluoride not even at 1200°. According to E. Petersen, the heat of neutralization $Zn(OH)_2+2HF_{aq.}$=25·10 Cals., and $Cd(OH)_2+2HF_{aq.}$=15·56 Cals.; O. Mulert gave for (CdO, 2HF)=23·48 cals. per mol; and, according to M. Berthelot, (Zn, F_2, aq.), 140 Cals.; and (Cd, F_2, aq.), 25·56 Cals. at 15°.

According to J. J. Berzelius, tetrahydrated zinc fluoride dissolves sparingly in water, but more readily in water acidified with hydrofluoric, hydrochloric, or nitric acid; a similar observation was made with cadmium fluoride, and A. Jäger explained the phenomenon by assuming that an acid or complex compound is formed. C. W. Scheele, and J. L. Gay Lussac and L. J. Thénard obtained **zinc hydrofluoride,** or **zinc acid fluoride,** by dissolving the normal fluoride in hydrofluoric acid, or zinc in an excess of the same acid. The solubility of cadmium fluoride in water at 25° is 0·289 mol. per litre—or 100 c.c. of a sat. aq. sol. of cadmium fluoride at 25° contain 4·36 grms. CdF_2—and in 10·8*N*-HF, 0·372 mol. per litre. Anhydrous zinc fluoride is very sparingly soluble in cold water. According to F. Kohlrausch and G. Bodländer, a litre of water dissolves 0·00005 mol. of zinc fluoride at 18°; and R. Dietz says a litre of water dissolves 16 grms. of $ZnF_2.4H_2O$ at 18°. Zinc and cadmium fluorides are insoluble in alcohol, and in hydrochloric, nitric, and sulphuric acids, but they dissolve in the boiling menstrua; cadmium fluoride is readily soluble in dil. mineral acids. When cadmium fluoride is evaporated with sulphuric acid, anhydrous cadmium sulphate is formed. Zinc or cadmium fluoride can be reduced by hydrogen; when heated in air, or with water vap., the metal oxide is formed. H. Schulze completely converted the fluoride into oxide by heating it in a stream of oxygen. Hydrogen sulphide transforms zinc or cadmium fluoride into the metal sulphide; and with hydrogen chloride, cadmium fluoride forms cadmium chloride. When zinc or cadmium fluoride is melted with alkali carbonate, alkali fluorides, and the metal oxide are formed; zinc fluoride with thionyl chloride, furnished M. Meslens with thionyl fluoride, SOF_2. According to H. Moissan, phosphorus tribromide converts zinc fluoride into bromide, but phosphorus trichloride has very little action, presumably because its volatility makes its mass action low.

Zinc fluoride is readily soluble in aqua ammonia, and it readily forms double salts with the alkali fluorides. R. Wagner, and H. von Helmolt prepared **ammonium zinc fluoride,** $2NH_4F.ZnF_2.2H_2O$, as a crystalline powder by the action of zinc hydroxide on a hot soln. of ammonium fluoride—ammonia is at the same time evolved. He also obtained similar results with cadmium fluoride; the product of the action is **ammonium cadmium fluoride,** $NH_4F.CdF_2$—almost insoluble in water, but soluble in boiling acids. R. Wagner made the same compound by the action of a soln. of ammonium fluoride in conc. aqua ammonia on freshly precipitated zinc oxide. R. Wagner made **sodium zinc fluoride,** $NaF.ZnF_2$, from a mixture of the component salts. J. J. Berzelius, and R. Wagner obtained crystals of **potassium zinc fluoride,** $KF.ZnF_2$, by evaporating a soln. of the component salts; C. Poulenc's analyses agree with $2KF.ZnF_2$.

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§ 12. Zinc and Cadmium Chlorides

According to H. Kopp, in his classical *Geschichte der Chemie* (Braunschweig, 1847), a mixture of zinc chloride was first described by J. R. Glauber, in his *De furnis novis philosophicis* (Amstelodami, 1648):

> *Oleum lapidis calaminaris* is obtained by digesting calamine in strong spirit of salt, and strongly heating the solution, whereby a *phlegma* is given off, and there remains a thick oil, as unctuous as olive oil, and not specially corrosive, because the *spiritus salis* has itself been weakened by dissolving the calamine, and thereby lost its sharpness. This *oleum* must be well protected from the air, otherwise, it attracts so much air as to form a watery liquid.

F. Stromeyer [1] first described cadmium chloride in 1818.

Other methods of preparing what came to be called *butter of zinc—beurre de zinc, butyrum zinci, Zinkbutter*—were discovered by J. H. Pott, J. Hellot, etc.[2] In 1782, F. A. Gallisch noticed that zinc forms a substance resembling butter when it is exposed to the action of dephlogisticated muriatic acid—chlorine—and in 1799 J. F. Westrumb found that finely divided zinc fires spontaneously in the same gas. R. Cowper, however, in 1883, observed that while the surface of zinc is attacked by chlorine which has passed through about 8 feet of one-inch tubing closely packed with anhydrous porous calcium chloride, it is *not* attacked if the chlorine be allowed to stand some days in contact with freshly fused calcium chloride. H. Davy also noted thin strips of zinc burn in chlorine gas with a white flame, forming zinc chloride; J. J. Berzelius made the same compound by passing dry chlorine over molten zinc—the action, he says, is attended by the emission of vivid sparks; and S. Grünauer says that with well-dried chlorine, and the purest available zinc, the reaction proceeds gradually. Zinc can also be chlorinated by heating it with twice its weight of mercuric chloride (J. H. Pott, 1741); with ammonium chloride (J. Hellot, 1735); with silicon chloride (N. N. Beketoff); with lead chloride (S. Grünauer); with phosphorus oxychloride (B. Reinitzer and H. Goldschmidt); and other chlorides of the metalloids. Many methods of preparation depend upon the volatility of zinc chloride, which, when anhydrous, boils between 700° and 730°; similar observations apply to cadmium chloride. This property enables the zinc chloride to be distilled from less volatile products. If iron be present, the ferric chloride distils first. G. P. Baxter and A. B. Lamb obtained anhydrous zinc chloride by heating ammonium zinc chloride in a stream of hydrogen chloride; and G. P. Baxter and M. A. Hines obtained anhydrous cadmium chloride in a similar manner. B. H. Jacobson found that a little bromine acts as a catalytic agent in the chlorination of zinc.

Hydrated zinc chloride crystallizes from its aq. soln. obtained by dissolving the metal, oxide, or carbonate in hydrochloric acid, or by treating soln. of the chlorides of metals which are precipitated by zinc—*e.g.* cupric chloride. According to R. Dietz, an aq. soln. can be evaporated to 80 per cent. $ZnCl_2$ at 50° over phosphorus pentoxide. R. Engel (1886) noticed that there are conditions when the anhydrous chloride can exist in contact with its aq. soln.; for example, F. Mylius

and R. Dietz found that an 85·5 per cent. soln. at 68° crystallizes at the room temp. in about 24 hrs., furnishing octahedral or prismatic crystals of zinc chloride; and the solubility curves, Fig. 29, show that the solid phase in aq. soln. over 28° is the anhydrous chloride. Like the other chlorides of this family, the evaporation of an aq. soln. of zinc chloride is attended by hydrolytic dissociation; so that, as noted by C. F. Wenzel in 1777, by heating a sat. soln. of zinc in hydrochloric acid, a part of the acid is expelled; and, as noted by J. Davy, a mixture of zinc chloride and oxide is obtained as a residue, but V. von Czepinsky and R. Lorenz showed that the product obtained even by melting zinc chloride, still contains a considerable amount of water, hydrogen chloride, or both. J. B. A. Dumas obtained cadmium chloride by evaporating a soln. of cadmium chloride in a stream of hydrogen chloride. Both J. H. Pott, and G. Brandt distilled zinc chloride from the residue obtained by evaporating an aq. soln. of zinc chloride to dryness—similar observations apply to cadmium chloride. W. L. Hardin sublimed the cadmium salt in a combustion tube in a stream of dry carbon dioxide.

C. Matignon and F. Bourion chlorinated *zinc oxide* by heating it in a stream of chlorine mixed with sulphur chloride vap.; K. J. Bayer treated zinc oxide suspended in water with chlorine: $6ZnO+6Cl_2=5ZnCl_2+Zn(ClO_3)_2$, and heated the resulting soln. with alkali chlorides, or treated the zinc oxide and alkali chloride together with chlorine until the last of the zinc oxide is dissolved. Many impurities are not chlorinated until after the zinc, and thus remain insoluble: $3ZnO+KCl+3Cl_2=3ZnCl_2+KClO_3$. The liquid when conc. to a sp. gr. 1·9 furnishes on cooling crystals of alkali chlorate. The mother liquid now contains very little chlorate, and it is treated with hydrochloric acid and evaporated to dryness to obtain zinc chloride. K. J. Bayer claims that there is a larger yield of chlorate with zinc oxide than when lime or magnesia is used, and that there is a large demand for the by-product, zinc chloride. E. Prior obtained zinc chloride as a by-product in the chlorinating roast of *zinc sulphide* ores mixed with sodium or calcium chloride and carbon, and subsequently volatilized at a higher temp.; G. Carrara applied a similar principle to chlorinating zinc oxides, carbonates, and hydrosilicates. E. H. Wikander made anhydrous zinc chloride by conducting a mixture of hydrogen chloride and air over zinc ferrous materials at a red heat. Wesenfeld, Dicke, & Co. chlorinated zinc oxide, sulphide, or carbonate, by mixing it with a soln. of ferric chloride. The excess of ferric chloride was then decomposed in the warm soln. by a current of air.

J. F. Persoz obtained anhydrous zinc chloride, by distilling a mixture of *zinc sulphate* and calcium chloride. C. Hensgen chlorinated zinc sulphate by the action of dry hydrogen chloride at 225°–250°; and by treating a soln. of zinc sulphate with the chloride of a metal which forms a sparingly soluble sulphate. Thus, D. C. Papenguth added calcium chloride to a soln. of zinc sulphate, and evaporated the filtrate; even sodium chloride will do at a temp. below 0°, for P. B. Sadtler and W. H. Walker applied A. J. Balard's process for Glauber's salt and cooled a soln. of zinc sulphate and sodium chloride whereby Glauber's salt crystallized out and zinc chloride remained in soln. They say that nearly a 100 per cent. yield can be obtained. According to F. Kessler, sodium zinc sulphate separates at 10° from a soln. containing a mol of zinc sulphate with two mols of sodium chloride; at 0°, Glauber's salt alone separates out and zinc chloride remains in soln. F. Käppel treated roasted zinciferous pyrites with sulphuric acid containing an excess of sodium chloride. The resulting soln. of zinc and sodium chlorides was treated with hydrogen chloride or conc. hydrochloric acid, free from the precipitated salt, and neutralized with zinc. In G. P. Baxter's work on atomic weights (*q.v.*) are described methods for the preparation of zinc and cadmium halides of a high degree of purity.

The properties of zinc and cadmium chlorides.—Molten zinc chloride is a soluble refracting fluid, and it congeals to a white vitreous or porcelain-like mass, which, according to R. Lorenz,[3] is more hygroscopic than phosphorus pentoxide. Molten cadmium chloride forms a white mass with a metallic lustre; according to

J. A. Wilkinson, if prepared by passing chlorine over molten cadmium, the colour is red—possibly from the presence of the colloidal metal. According to M. Gröger, the sublimed salt forms transparent mica-like plates; W. L. Hardin obtained plate-like crystals resembling mother-of-pearl; white needles have been reported; and G. Viard obtained granular crystals. O. Lehmann studied the crystals of this salt; the crystal system is probably hexagonal. R. Dietz found the anhydrous crystals formed as solid phase in aq. soln. over 28° are octahedral or prismatic. E. F. Farnau studied the **crystalloluminescence** of the zinc and cadmium halides.

According to H. C. D. Bödeker,[4] anhydrous zinc chloride has a **specific gravity** of 2·753 (13°), while G. P. Baxter and A. B. Lamb, as a mean of five determinations, give the mean value 2·907 at 25° (water unity). For anhydrous cadmium chloride H. C. D. Bödeker gives 3·6354 (12°); F. W. Clarke, 3·655 (16·9°) and 3·938 (23°); and G. P. Baxter and M. A. Hines, as a mean of five determinations, 4·047 at 25° (water unity). R. Lorenz, H. Frei, and A. Jabs give for the sp. gr. D of molten cadmium chloride at θ between 600° and 800°, $D=6{\cdot}175-0{\cdot}00145\theta$. Assuming the best representative sp. gr. of zinc and cadmium chlorides are respectively 2·91 and 4·05, the respective mol. vols. are 46·9 and 45·3. W. Biltz gave 45·18 for the mol. vol. of cadmium chloride. A. J. Rabinowitsch measured the sp. gr. of soln. of the last-named salt; as also the viscosity.

The reported numbers for the **melting point** of anhydrous zinc chloride vary from R. Lorenz's [5] 250° to K. Hachmeister's 283°. The reason for the large difference is probably due to the more or less imperfect dehydration of the salt used in the determination; for anhydrous cadmium chloride the numbers vary from L. Graetz's 538° to O. H. Weber's 590°. The best representative values may be taken as 290° for zinc chloride, and 568° for cadmium chloride. O. Ruff and W. Plato obtained a minimum in the m.p. curve of mixtures of cadmium fluoride and chloride at about 540° and 84 molar per cent. of the chloride, Fig. 28. Likewise, the **boiling point** of anhydrous zinc chloride is 730°, according to V. Meyer and F. Freyer; T. Carnelley and W. C. Williams' data ranged from 716° to 730°; and for anhydrous cadmium chloride from 861° to 954°—O. H. Weber gives 964°. The best representative values are 730° for zinc chloride and 960° for cadmium chloride. C. Zenghelis says that zinc chloride evaporates at ordinary temp. because a piece of zinc chloride after standing over a silver plate 5 cms. away for five days produced a grey film on the metal. According to V. and C. Meyer,[6] the **vapour density** of zinc chloride at 891° is 4·53; and at 907°, 4·61; while the value calculated for $ZnCl_2$ is 4·70. A. Werner determined the mol. wt. in organic solvents. E. Beckmann found the mol. wt. of zinc chloride in boiling quinoline to be virtually normal 139 when the calculated value for $ZnCl_2$ is 136·3; N. Castoro also found a normal value for the f.p. of urethane; R. Lespieau found high values for the f.p. of ether representing polymerization with mol. wt. 230, 280, and 540. E. Beckmann obtained a mol. wt. 185 for soln. of cadmium chloride in boiling quinoline, the calculated value for $CdCl_2$ is 183; L. Rügheimer, in boiling bismuth trichloride, 187·3 to 193·1; G. Tammann obtained abnormal values for the lowering of the vap. press. of soln. of cadmium chloride in water; J. L. R. Morgan and H. K. Benson obtained 158 for the mol. wt. of cadmium chloride in fused trihydrated lithium nitrate. A. Werner found the solubility in piperidine to be too low to enable a mol. wt. determination to be made.

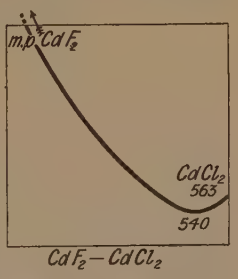

FIG. 28.—Fusion Curve of Mixtures of Cadmium Fluoride and Chloride.

O. H. Weber [7] calculated the **heat of fusion** of cadmium chloride to be 10·5 Cals. and the **heat of vaporization,** 26·0 Cals. H. V. Regnault found the **specific heat** of vitreous zinc chloride between 21° and 99° to be 0·1362; C. Helmreich gives for

cadmium chloride between 0° and 30°, 0·09362 ; between 0° and 50°, 0·09533 ; and between 0° and 70°, 0·09701. According to J. C. G. de Marignac, the sp. and mol. ht. of soln. of zinc chloride between 19° and 51° are for soln. with a mol of salt :

Mols of H_2O .	10	15	25	50	100	200
Sp. ht. .	0·6212	0·7042	0·7960	0·8842	0·9330	0·9590
Mol. ht. .	196·5	286·1	466·7	916·0	1807	3583

A. Blümcke has also measured the sp. ht. of soln. of zinc chloride, and C. Helmreich of soln. of cadmium chloride :

Per cent. $CdCl_2$ . .	17·12	32·15	47·65
Sp. ht. 0° to 30° . .	0·83149	0·80956	0·81409
Sp. ht. 0° to 50° . .	0·70187	0·69174	0·69419
Sp. ht. 0° to 70° . .	0·56910	0·56367	0·56577

G. Jäger found the **heat conductivity** of water is reduced approximately 0·00473 for each per cent. of zinc chloride in soln. The heat conductivity of a 17·5 per cent. soln. of zinc chloride is 91·5 (water 100), and of a 35 per cent. soln., 83·7. W. Beetz's values for the absolute conductivities of soln. of sp. gr. 1·132 and 1·870 are respectively 0·00436 and 0·00370 between 8° and 14° ; and 0·00660 and 0·00445 between 36° and 28°.

J. Thomsen [8] found the **heat of formation** (Zn, Cl_2) to be 97·2 Cals., and M. Berthelot, 97·2 Cals. ; R. de Forcrand, 98·73 Cals. ; and R. Lorenz from 428° to 608°, 95·547 Cals. V. von Czepinsky calculates the mol. ht. of formation to be 95·869 Cals. at 408° ; 96·101 Cals. at 468° ; and 185·146 Cals. at 688° ; and from J. Thomsen's value for the heat of formation, he gives the heat of formation at 408° as $95·902-Q$, and at 468°, $97·59-Q$, where Q denotes the unknown mol. ht. of fusion. E. E. Somermeier found the heat of dissolution of zinc in $HCl+191·5H_2O$ to be 30·43 Cals. per gram-atom ; and T. W. Richards and T. Thorvaldson, $Zn+2(HCl, 200H_2O)=ZnCl_2.400H_2O+H_2$ to be 36·32 Cals. for dry hydrogen and 36·07 Cals. for moist hydrogen at 20°. The total energy change, U, is 36·90 Cals. at 20° ; the temp. coeff. is negative, probably —0·030 Cal. per degree. T. W. Richards and S. Tamaru found $Cd+2(HCl, 200H_2O)=CdCl_2.400H_2O+H_2$ at 20° to be 17·23 Cals. with dry hydrogen, and 16·98 Cals. with moist hydrogen. $U=17·81$ Cals. at 20° ; and the temp. coeff. is negative, —0·071 Cal. per degree with conc. acid, and —0·030 Cal. per degree with dil. acids. J. Thomsen also gave (Zn, Cl_2, aq.), 112·3 Cals. ; (Cd, Cl_2), 93·2 Cals., a number in agreement with M. Berthelot's value. H. S. Taylor and G. S. J. Perrott give 93·8 Cals. for the heat of formation of cadmium chloride from its elements. J. Thomsen also gives (Cd, Cl_2, 2aq.), 95·49 Cals. ; and for ($CdCl_2$, $2H_2O$), 2·25 Cals. R. Lorenz and M. G. Fox calculate 86·8 Cals. for the heat of formation of molten cadmium chloride between 560° and 740°. The crystals of zinc chloride have a strong affinity for water, and they deliquesce rapidly in air. J. Thomsen's value for the **heat of solution** of a mol of zinc chloride in 400 mols of water at 18° is 15·63 Cals. ; and for cadmium chloride, 3·01 Cals. ; M. Berthelot's value for cadmium chloride at 10° is 3·0 Cals. The heat of soln. for $CdCl_2.H_2O$ is 0·625 Cal., and for what was thought to be $CdCl_2.2H_2O$, —2·28 Cals. S. U. Pickering's value for the heat of soln. of zinc chloride is 15·22 Cals. J. Thomsen's values for the **heat of dilution** of a soln. of a mol of zinc chloride in 5 mols of water until the whole soln. contains 10, 100, and 400 mols of water are respectively 1·849, 6·809, and 8·02 Cals. C. R. A. Wright and C. Thompson's values for the heat of dilution of $xZnCl_2+100H_2O$ to $0·25ZnCl_2+100H_2O$ for $x=0·5$, 0·4 Cal. per mol ; for $x=5$, 4·8 Cals. ; and for $x=25$, 9·0 Cals. per mol. According to W. Nernst, conc. soln. of zinc chloride are *ideal* in the sense that the heat of dilution is eq. to the change of free energy on dilution. C. R. A. Wright and C. Thompson also find the heat developed in diluting $5CdCl_2+100H_2O$ to $0·25CdCl_2+100H_2O$ is 0·1Cal. per mol. J. Thomsen also found the **heat of neutralization** $Zn(OH)_2+2HCl$ in very dil. soln. to be 19·881 cals., and of $Cd(OH)_2+2HCl$, 20·295 cals. H. Schultze [9] found the **electrical conductivity** of solid zinc chloride at 230° to be 0·000008.

In 1830, R. Schindler [10] analyzed zinc chloride and deduced the formula $ZnCl_2.2H_2O$, and R. Engel described three hydrates which he believed to be $ZnCl_2.1\frac{1}{2}H_2O$, $ZnCl_2.2H_2O$, and $ZnCl_2.3H_2O$. The work of F. Mylius and R. Dietz has thrown considerable light on the character of the hydrates of zinc chloride. F. Mylius and R. Dietz's solubility curves of zinc chloride in water are shown in Fig. 29. The curves between 0° and 30° were quite complex, since several hydrates may exist. In all, there are hydrates $ZnCl_2H_2O$; $ZnCl_2.1\frac{1}{2}H_2O$; $ZnCl_2.2\frac{1}{2}H_2O$; $ZnCl_2.3H_2O$; and $ZnCl_2.4H_2O$. R. Engel reported *dihydrated zinc chloride*, $ZnCl_2.2H_2O$, to be formed by cooling in ice a 79·9 per cent. soln. of zinc chloride. R. Dietz (1899), and A. Étard (1894) also described the preparation of this salt. H. Lescœur (1894) also says the vap. press. curve of hydrated zinc chloride corresponds with this hydrate, but the later work of F. Mylius and R. Dietz (1905) has thrown a doubt on its existence, for they say that tetrahydrated zinc chloride, $ZnCl_2.4H_2O$, is the solid phase in aq. soln. below −30°. The eutectic with ice and tetrahydrated zinc chloride occurs at −62°, when the soln. has 51 per cent. of $ZnCl_2$. The solubility curve rises from *A* to *B* at −30° when the soln. has 61·5 per cent. $ZnCl_2$; trihydrated zinc chloride, $ZnCl_2.3H_2O$, now appears as a solid phase. The transition point: $ZnCl_2.4H_2O \rightleftharpoons ZnCl_2.3H_2O + H_2O$, is at −30°. The solubility of trihydrated zinc chloride at 0°, is 67·5 per cent., and following the curve *BCD*, the trihydrated salt melts at *C*, 6·5°, 71·6 per cent. $ZnCl_2$, and falls to the eutectic *D*, 0°, when the solubility is 75·5 per cent. $ZnCl_2$, and the solid phases are trihydrated zinc chloride and sesquihydrated zinc chloride, $ZnCl_2.1\frac{1}{2}H_2O$, which appears as a new solid phase. A transition point appears at 26°, *H* in the solubility curve of the sesquihydrated salt, *DFH*, when the soln. contains 80·9 per cent. $ZnCl_2$. A new phase zinc monohydrated chloride, $ZnCl_2.H_2O$, now appears. The solubility curve of the triaquo-salt may take a course different from *BCD* for the solid phase at *C*, about 6·5°, may suffer a change; *C* becomes a transition point, and a new phase, hemipentahydrated zinc chloride, $ZnCl_2.2\frac{1}{2}H_2O$, may appear, and the solubility curve of this salt is represented by *CEF*; at 12·5°. *E*, this salt melts, and there is 75·2 per cent. of $ZnCl_2$ in soln.; at the eutectic 11·5°, *F*, 77 per cent. $ZnCl_2$, there are the solid phases hemipentahydrated zinc chloride and the new phase zinc sesquihydrated chloride, $ZnCl_2.1\frac{1}{2}H_2O$. The solubility curve of the sesquihydrated salt, *FH*, has a transition point at 26°, *H*, 80·9 per cent. $ZnCl_2$ when the solid phase is zinc sesquihydrated chloride, $ZnCl_2.1\frac{1}{2}H_2O$, and the new phase monohydrated zinc chloride, $ZnCl_2.H_2O$. The solubility curve of the monohydrated chloride has a transition point, *J*, 26·3°, when the soln. has 81·2 per cent. of $ZnCl_2$, and solid phases monohydrated zinc chloride, and the new phase, anhydrous zinc chloride $ZnCl_2$, whose solubility curve, represented by *JV*, terminates at 262°, the m.p. of anhydrous zinc chloride:

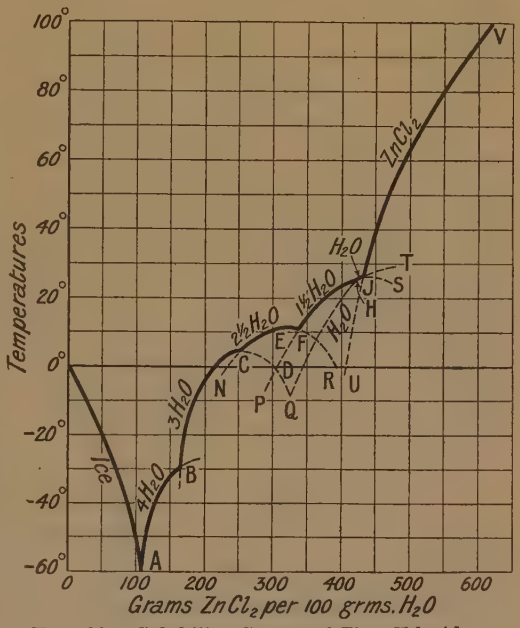

FIG. 29.—Solubility Curves of Zinc Chloride.

	26·3°	40°	60°	80°	100°	262°
Per cent. $ZnCl_2$. . .	81·2	81·9	83·0	84·4	86·0	100·0

The unstable regions of the solubility curve are dotted in the diagram.

The highest hydrated salt : **tetrahydrated zinc chloride,** $ZnCl_2.4H_2O$, was prepared by F. Mylius and R. Dietz in large prismatic crystals by cooling a 65·4 per cent. soln. below −30°. The solubility curve has been plotted, Fig. 29, from the transition point −30° down to the eutectic with ice at −62°, although undercooled soln. down to −70° have been obtained. Very hygroscopic rhombic plates, and cubic crystals of **trihydrated zinc chloride,** $ZnCl_2.3H_2O$, resembling sodium chloride have been obtained by R. Engel by keeping a 70·5 per cent. soln. of zinc chloride at 0° for 24 hrs. The crystallization starts when the soln. has been allowed to stand a few hours. F. Mylius and R. Dietz obtained the same result by keeping a 70·5 per cent. soln. between −10° and −15° for 2 or 3 hrs. and rubbing on the vessel with a glass rod ; H. C. Jones and H. P. Bassett, at −17° ; E. Lubarsky, at −21°. The m.p. is given between 4° and 7°. The range of stability and solubility is indicated in the diagram. R. Dietz made **hemipentahydrated zinc chloride,** $ZnCl_2.2\frac{1}{2}H_2O$, in rhombic plates by cooling a 74 per cent. soln. to 0°, or a 75·2 per cent. soln. to −10° and rubbing on the bottom of the vessel with a glass rod. The crystals are stable between 6° and the m.p., 12·5° or 13°. R. Dietz made deliquescent prismatic crystals of **sesquihydrated zinc chloride,** $ZnCl_2.1\frac{1}{2}H_2O$, by cooling a neutral 83 per cent. soln. to 0°, warming the crystalline mass to 20°, and transferring the crystals to a 81 per cent. soln. F. Mylius and R. Dietz also obtained the crystals by cooling a 83·5 per cent. soln. R. Engel made the crystals by evaporating in a desiccator over phosphorus pentoxide, the mother liquor remaining after the crystallization of a 79·9 per cent. soln. The crystals melt at 26°—according to R. Engel, the heat of the hand suffices to melt them. By mixing hydrochloric acid with a syrupy soln. of zinc chloride, R. Schindler obtained deliquescent hexagonal plates which R. Dietz showed to be **monohydrated zinc chloride,** $ZnCl_2.H_2O$; and the latter obtained similar crystals by slowly cooling a 86 per cent. neutral soln. and transferring the crystal mass to a 82 per cent. soln. ; F. Mylius and R. Dietz obtained the crystals by allowing a 83·5 per cent. soln. to stand many days ; and H. C. Jones and H. P. Bassett obtained the same salt by crystallization at a high temp. The range of stability shown in Fig. 29 is small—between 26° and 28°.

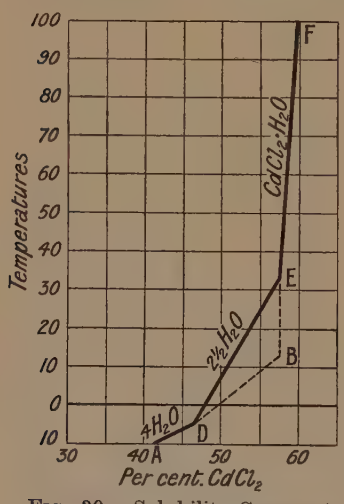

Fig. 30.—Solubility Curves of Cadmium Chloride.

A. Stromeyer[11] in 1818, and F. J. John in 1819, described a hydrate of cadmium chloride which J. J. Berzelius believed to be *dihydrated cadmium chloride,* $CdCl_2.2H_2O$. R. Dietz believes that the so-called dihydrated salt of the older investigators is the hemipentahydrated salt, but, as K. Drucker remarks, the existence of R. Dietz's hemipentahydrated salt cannot be regarded as *über alle Zweifel.* The *heptatritahydrated cadmium chloride,* $CdCl_2.2\frac{1}{3}H_2O$, of H. Grossmann and B. Schück is probably either the di- or hemipentahydrated salt. R. Dietz's curves of the solubility of cadmium chloride from −9° to 100° are shown in Fig. 30. It is simpler than that of zinc chloride. R. Dietz's data up to 100°, and A. Étard's from 120° to 277°, are :

	−9°	−5°	0°	30°	34°	40°	100°	120°
Per cent. $CdCl_2$, .	43·6	46·2	47·4	56·3	57·4	57·5	59·5	63·0
Solid phases . . .	$CdCl_2.4H_2O$	⇌	$CdCl_2.2\frac{1}{2}H_2O$		⇌	$CdCl_2.H_2O$		

and at 170°, 68·4 per cent. ; at 200°, 72 per cent. ; and at 270°, 77·7 per cent. $CdCl_2$. At the two transition points *D*, −5°, and *E*, 34°, there are two solid phases in the former case, $CdCl_2.4H_2O$ and $CdCl_2.2\frac{1}{2}H_2O$; and in the latter case, $CdCl_2.2\frac{1}{2}HO$ and $CdCl_2.H_2O$. The unstable extension of the solubility curve of the tetrahydrated salt *AD* is the dotted line *DB*. At *B*, 12·5°, the soln. has 57·3 per cent. of $CdCl_2$, and here the two solid phases are $CdCl_2.4H_2O$ and $CdCl_2.H_2O$. The unstable region in the solubility curve of the monohydrated salt is represented by the dotted line *BE*.

N. Worobieff reported the formation of *pentahydrated cadmium chloride*, $CdCl_2.5H_2O$, by cooling a 50 per cent. soln. of cadmium chloride to $-14°$, and drying the crystals between blotting paper. He adds that the crystals melt between 21·5° and 22°. R. Dietz failed to confirm the existence of this salt, but H. Lescœur and R. Dietz have shown the conditions under which **tetrahydrated cadmium chloride**, $CdCl_2.4H_2O$, is formed, and its solubility is indicated in Fig. 30. Some of the older reports of dihydrated cadmium chloride really apply to this salt. According to S. U. Pickering, F. von Hauer, and others. *dihydrated cadmium chloride*, $CdCl_2.2H_2O$, is formed when soln. of cadmium chloride are evaporated at ordinary temp., and, according to N. Worobieff, when soln. are crystallized at 100°. According to R. Dietz, and K. Sudhaus, the salt is really **hemipentahydrated cadmium chloride.** The solubility curve is indicated in Fig. 30. It is transformed into monohydrated cadmium chloride at 34° (R. Dietz); at 33° to 33·72° by dilatometric measurements, or at 34·1° by electrometric measurements (E. Cohen). J. Thomsen gives its heat of formation as 95·49 Cals. and its heat of soln. in 400 mols of water at 18° is 0·76 Cal.; and, according to S. U. Pickering, its heat of soln. is 2·284 Cals. According to A. Fock, the crystals are isomorphous with dihydrated barium chloride. The crystals were once stated to be rhombic, but R. Dietz said that they are monoclinic with axial ratios $a:b:c = 0·4181:1:?$ and with $\beta = 91° 27'$. According to S. U. Pickering, and E. Cohen, the evaporation of a soln. at a high temp. furnishes fine needle-like or columniar crystals of **monohydyated cadmium chloride,** $CdCl_2.H_2O$. H. Lescœur made the same salt by evaporating the mother liquid remaining after the tetrahydrated salt has crystallized out; and G. Viard, by precipitation from a soln. of cadmium chloride by the addition of a not too great excess of sulphuric acid. H. Lescœur obtained evidence of its existence from the vap. press. curves, and he says its dissociation press. is about 50 mm. at 80°, 151 mm. at 100°, and 232 mm. at 110°, and, according to G. Viard, it passes into the anhydrous salt if kept in vacuo for a long time. The heat of soln., according to S. U. Pickering, is 0·625 Cal. The solubility curve and range of stability are shown in Fig. 30.

The **specific gravities** of aq. soln. of zinc chloride have been determined by P. Kremers,[12] C. Bender, F. Kohlrausch, D. I. Mendeléeff, D. Dijken, J. H. Long, V. S. M. van der Willigen, etc. J. H. Long's data at 15° are:

Per cent. $ZnCl_2$.	0·5994	2·50	4·89	10·00	20·00	29·86	40·00	58·88
Sp. gr. . .	1·00056	1·024	1·046	1·094	1·094	1·297	1·423	1·728

The value for the 0·5994 per cent. soln. is by D. Dijken. J. Wagner's values at 25° for N-, $\frac{1}{2}N$-, and $\frac{1}{4}N$-soln. are respectively 1·0590, 1·0302, and 1·0017. P. Kremers, C. A. Valson, J. Wagner, H. Jahn, F. J. Wershoven, S. Oppenheimer, etc., have likewise measured the sp. gr. of soln. of cadmium chloride. E. Biron's percentage values, p, at $20° \pm 0·03°$ (water at 4° unity) are:

Per cent. $CdCl_2$.	0·849	5·01	8·046	16·65	28·61	32·52	46·49	51·21
Sp. gr. . . .	1·0062	1·0437	1·0720	1·1613	1·3090	1·3659	1·6011	1·7020

The first two values are by O. Grotrian at 18°. E. Biron's results are very well represented by the interpolation formula: $D = 0·9983 + 0·0087144p + 0·0000474p^2 + 0·000000991p^3$. F. Fouqué has measured the change in the sp. gr. of zinc chloride soln. with temp.; P. Kremers, the vol. occupied by cadmium zinc chloride soln. of different conc.; and G. Happart showed that the contraction which occurs during the soln. of solid zinc chloride, sp. gr. 2·753 (15°), to form 100 c.c. of a p per cent. soln., is: Contraction $= 0·00244(100-p)p$; and for cadmium chloride: Contraction $= 0·00114(100-p)p$. According to W. Ostwald, a normal soln. of zinc chloride has the sp. vol. 0·969286. M. L. Frankenheim represents the vol., v, of a soln. at θ by the expression: $v = 1 + 0·0005435\theta + 0·0000013\theta^2$, and both P. Kremers and C. Forch have measured the thermal expansion of soln. of different conc., and found for $\frac{1}{2}N$-, N-, and $2N$-soln. between 0° and 5°, respectively, 0·000044, 0·000118 and 0·000271; between 5° and 10°, 0·000106, 0·000173, and 0·000315; between 10° and 15°, 0·000164, 0·000228, and 0·000354; between 15° and 20°, 0·000216, 0·000279, and 0·000398; between 20° and 25°, 0·000265, 0·000323, and 0·000434; between 25° and 30°, 0·000309, 0·000367, and 0·000467; between 30° and 35°, 0·000351, 0·000410, and 0·000504; between 35° and 40°, 0·00396, 0·000447, and 0·000526.

The **viscosities** of soln. of zinc and cadmium chlorides have been measured by J. Wagner,[13] and he finds (water unity):

		N-	½*N*-	¼*N*-	⅛*N*-
Viscosity	$ZnCl_2$	1·1890	1·0959	1·0526	1·0238
	$CdCl_2$	1·1342	1·0631	1·0310	1·0202

O. Pulvermacher also studied the viscosity of soln. of zinc chloride. According to F. Mylius and R. Dietz, the viscosity of the syrupy soln. of zinc chloride increases rapidly as the temp. falls such that at −70°, it is brittle like glass, and at the temp. of liquid air, owing to irregular contraction, numerous crazes appear, but no crystallization occurs. G. Foussereau's value for the viscosity coeff. of molten zinc chloride at 262° is 50·9, and at 301°, 34·7. The **capillary constants** of soln. of zinc and cadmium chlorides have been measured by C. A. Valson,[14] E. Klupathy, M. L. Frankenheim, etc. At 15°, C. A. Valson found a soln. containing w grms. of $ZnCl_2$ in 100 grms. of water to ascend a height of h mm. in a tube 0·5 mm. diameter; and for $CdCl_2$ a height h in a tube of 0·25 mm. diameter:

w	0	5	10	15	20	25	30
$h(ZnCl_2)$	60·6	58·7	56·9	55·3	53·9	52·6	51·6
$h(CdCl_2)$	60·6	58·5	56·3	54·5	53·0	51·9	—

The capillary constants of molten zinc and cadmium chlorides have been measured by G. Quincke. According to S. Motylewsky, the drop-weights, W, of zinc and cadmium chlorides at their m.p. are respectively 72 and 105, where the **surface tension**, σ, is $\sigma=0·076W$; and the **specific cohesion** $a^2=26/D$, where D is the sp. gr. at the m.p. The surface tensions of soln. of zinc chloride between 0° and 25° were found by H. Sentis to be independent of the temp. According to J. C. Graham, the **velocity of diffusion** of 3 to 5 per cent. soln. of zinc chloride against water is 0 628; and, according to P. de Heen, it is not very different for soln. between 1 and 10 per cent. conc. According to H. de Vries, the rate of diffusion in gelatin is 2·45 sq. cm. per day.

The **vapour pressures** of soln. of zinc chloride have been measured by J. Moser,[15] J. Walker, G. Tammann, and H. Lescœur, and of cadmium chloride by H. Lescœur and G. Tammann. According to J. Moser's data, at 20·2° for w grms. of $ZnCl_2$ per 1000 grms. of water when $w=250$, $dp=1·44$, $dp/p=0·082$, and $dp/pw=0·00033$; and when $w=1250$, $dp=9·55$, $dp/p=0·560$, and $dp/pw=0·00045$; for cadmium chloride at 100°, G. Tammann's numbers give $w=0·5$, $dp=9·6$, $dp/p=0·0126$, and $dp/pw=0·0252$; and for $w=5$, $dp=99·0$, $dp/p=0·130$, and $dp/pw=0·0260$. H. Lescœur found for a sat. soln. of cadmium at 20°, a vap. press. of 12·2 mm.; for $CdCl_2+4·5H_2O$, 11·0 mm.; for $CdCl_2+3·5H_2O$, 10·5 mm.; $CdCl_2+1·5H_2O$, 7 mm.; $+1·07H_2O$, 6·5 mm.; $+1·01H_2O$, 6·2 mm.; and $+0·96$ below 2 mm. This shows a significant indication of the existence of a monohydrated salt.

The **lowering of the freezing point** of dil. soln. of zinc chloride has been investigated by H. C. Jones[16] and co-workers, and by W. Biltz, and the results show that J. H. van't Hoff's constant i falls from 2·91 for soln. with 0·001 mol per litre, to $i=2·49$ for soln. with 0·0819 mols per litre. H. C. Jones and co-workers, and W. Kistiakowsky obtained similar results with soln. of cadmium chloride. L. Kahlenberg and co-workers investigated the effect of cane sugar on the results. S. M. Johnston, and A. Benrath also measured the **raising of the boiling point** of water by cadmium chloride.

The **refractive indices** of soln. of zinc and cadmium chlorides have been measured by numerous investigators.[17] According to C. Cheneveau, at 16° the refractive index for the sodium-line for water alone is 1·3512, and this rises from 1·3592 to 1·380 for soln. respectively with 9·39 and 30·95 per cent. of zinc chloride; and for cadmium chloride soln. at 15°, R. de Muynck found the refractive index to rise from 1·35835 to 1·47314 as the conc. of the soln. rose from 0·159 to 0·629 mol of $CdCl_2$ per 100 grms. of soln. According to V. S. M. van der Willigen, for soln. of zinc chloride with light of different wave-lengths at 19·5°:

Sp. gr.	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
1·35949	1·39690	1·39884	1·39977	1·40222	1·40532	1·40797	1·41297	1·41738
1·20930	1·37038	1·37210	1·37292	1·37515	1·37789	1·38026	1·38465	1·38845

The **dispersions** of soln. of zinc chloride with 2·0687 and 32·822 grms. per 1000

grms. of soln. are respectively $(\mu_\alpha-\mu_\beta)/(\mu_D-1)=0{\cdot}0307$ and $0{\cdot}0305$ at 16°; and for cadmium chloride with $0{\cdot}1954$ and $0{\cdot}3765$ grm. per c.c., $\mu_\alpha=1{\cdot}3577$ and $1{\cdot}3884$ respectively; $\mu_\beta=1{\cdot}3646$ and $1{\cdot}3964$; and $\mu_D=1{\cdot}3599$ and $1{\cdot}3908$. According to H. Jahn, the **electromagnetic rotation** of the plane of polarization for soln. of zinc chloride of sp. gr. $1{\cdot}3200$ to $1{\cdot}1500$ (20°) is $1{\cdot}1535$; and for soln. of cadmium chloride of sp. gr. $1{\cdot}081$ to $1{\cdot}5645$ (20·5°), is $1{\cdot}14$ to $1{\cdot}15$. According to P. D. Foote and F. L. Mohler, the **ionization potential** of zinc chloride vapour is 12·9 volts. E. J. Evans studied the **absorption spectrum** of cadmium chloride vapour. J. R. Collins measured the ultra-red absorption spectrum of aq. soln. of zinc chloride.

According to G. Foussereau,[18] the **specific resistance** of solid zinc chloride, in ohms per c.c., is $0{\cdot}0107\times10^6$ at 171°, and 2370×10^6 at 59°, and the change of resistance R with temp. is: $\log R=13{\cdot}268-0{\cdot}07304\theta+0{\cdot}0001112\theta^2$. L. Graetz gives the **electrical conductivity** of the solid (mercury unity), 2×10^{-8} at 230°; 5×10^{-8} at 240°; 10×10^{-8} at 250°; and 16×10^{-8} at 260°. M. Faraday and W. Hampe find molten zinc chloride to be a very good conductor of electricity. G. Foussereau gives $R=31{\cdot}1900-1646\theta+0{\cdot}0002366\theta^2$; and L. Graetz, the conductivity (mercury unity), 100×10^{-8} at 262°, and 1450×10^{-8} at 300°; and H. S. Schultze measured the conductivity over the range from 700° to 225°, and found it to fall rapidly with temp. Expressing the results resistance, R, in ohms per c.c.:

	700°	500°	300°	270°	260°	250°	225°
R	0·460	0·104	0·00186	0·00022	0·00011	0·000026	0·000006

The conductivity of cadmium chloride, according to L. Graetz, is:

	580°	538°	530°	500°	490°	430°	420°	370°
$R\times10^8$	1470	1140	980	100	75	22	19	7

The electromotive force of the cell Zn | $ZnCl_{2molten}$ | Zn is $0{\cdot}00013(\theta_1-\theta_2)$, where θ_1 is greater than θ_2. At 500°, R. Lorenz found with carbon electrodes molten zinc chloride decomposed between 1·49–1·50 volts, and in carbon dioxide at 467°, at 1·505 volts. When heated to 360°, A. E. Garrett found zinc and cadmium chlorides ionized the surrounding gas; and the energy necessary for the ionization of a mol of zinc chloride at 335° is 165 Cals. nearly.

Many measurements have been made of the eq. electrical conductivities of soln. of zinc and cadmium chlorides. A. Heydweiller[19] found for soln. of n mols of zinc chloride per litre, and O. Grotrian, and F. J. Wershoven for cadmium chloride, at 18°:

n	0·05	0·1	0·2	0·5	1·0	2·0	3·0	4·0	9·0
λ-$ZnCl_2$	—	84·8	77·7	67·3	55·1	38·9	29·2	22·5	—
λ-$CdCl_2$	91·0	50·0	41·2	30·8	22·4	14·4	9·9	7·2	1·4

The fall in the eq. conductivity of zinc chloride with increasing conc. is in accord with the values obtained for the chlorides of magnesium and the alkaline earths, and hence the character of the ions is approximately the same. The complex ions present are therefore less than is the case with soln. of cadmium chloride where the eq. conductivity changes more rapidly with conc. H. C. Jones and co-workers gave for the mol. conductivity, μ, and the percentage degree of ionization, α, with soln. containing a mol of cadmium chloride in v litres of soln.:

v	4	8	32	128	512	2048
μ_0°	23·65	45·32	65·63	88·34	106·14	121·19
μ_{65}°	106·5	139·6	216·2	300·0	378·8	440·5
α_0°	27·8	37·4	52·2	72·9	87·6	100·0
α_{65}°	24·2	31·7	49·1	68·1	86·0	100·0

The *temperature* coeff. of the conductivity of zinc chloride soln. has been determined by F. Kohlrausch, J. H. Long, S. Lussana, S. Arrhenius, and H. C. Jones and co-workers; and the effect of *pressure* by B. Piesch, and S. Lussana. A. J. Rabinowitsch studied the anomalous ionization—*i.e.* the decrease in conductivity with dilution of cadmium chloride.

The **transport number** of the anions of aq. soln. of zinc chloride has been measured by F. Kohlrausch,[20] W. Hittorf, G. Kümmell, and J. Moser; W. Hittorf found that with soln. containing 1·3458, 2·7005, and 53·988 grms. of water per gram of cadmium chloride in cells without a diaphragm, the respective transport numbers are 0·556, 0·555, 0·565 for the anions, and 0·444, 0·445, and 0·435 for the cations; and for soln. with a 2·7736 and 332·87 grms. of water per gram of zinc chloride, W. Hittorf found the transport numbers of the anion to be respectively 1·08 and 0·700; while G. Kümmell obtained 0·603 for soln. with from 0·0013 to 0·0051 mols $ZnCl_2$ per litre. It therefore follows that for conc. soln. of zinc chloride, a comparatively large proportion of the zinc travels to the anode as a complex ion. G. N. Lewis and M. Randall calculated the activity coeff. of the ions of cadmium chloride. The **degree of ionization** of soln. of zinc and cadmium chlorides has been calculated by A. A. Noyes,[21] H. C. Jones, S. Labendzinsky, etc. There is a fall from 92·1 to 74·4 per cent. ionization respectively for 0·001*N*- and 0·0819*N*-soln. of zinc chloride; and from 82·3 to 53·7 per cent. respectively for 0·366*N*- and 20·976*N*-soln. of cadmium chloride. A. Günther-Schulze studied the ionization of cadmium chloride in aq. soln.

The **electromotive force** between two soln. with n and m mols of zinc chloride per 100 mols of water was measured by C. R. A. Wright and C. Thompson [22] with electrodes of zinc amalgam, and also by J. Moser. The former found when m=24·4, and n=9·8, the e.m.f.=112·0; when m=24·4, n=2·04, the e.m.f.=218·1; and when m=3·3, n=2·04, the e.m.f.=11·0; when m=24·4, n=0·172, the e.m.f.=259·0; when m=3·3, n=0·172, the e.m.f.=51·9; and when m=0·25, n=0·172, the e.m.f.=4·9. The potential of zinc in soln. of zinc chloride against a normal calomel electrode is 1·062, 1·090, and 1·104 volts respectively for N-, $\frac{1}{10}N$-, and $\frac{1}{100}N$-soln. of $ZnCl_2$. Similar results have been obtained with soln. of cadmium chloride by C. R. A. Wright and C. Thompson. T. des Courdes, E. Bouty, A. Hagenbach, etc. The temp. coeff. as well as the electromotive force of various voltaic combinations have likewise been measured. J. Königsberger [23] found the **magnetic susceptibility** of aq. soln. of zinc and cadmium chlorides, at 22°, to be $0·50\times10^{-6}$ (air zero) units of mass; and S. Meyer the magnetic susceptibility of powdered cadmium chloride at 18° to be $-0·25\times10^{-6}$ (air zero).

Zinc chloride is used as a preservative for wood. In 1918, 31,101,111 lbs. were used for this purpose in the United States. G. Wood [24] showed that sodium fluoride offers some advantages over zinc chloride, and G. M. Hunt thus summarizes the relative advantages of these two preservatives:

> Solubility in water: zinc chloride is soluble in all proportions; sodium fluoride is soluble to about 4 per cent. Toxicity: zinc chloride is toxic enough to increase materially the life of wood; sodium fluoride is over twice as toxic as zinc chloride. Corrosive effect on steel: zinc chloride is somewhat corrosive, but is commonly used in steel apparatus; sodium fluoride is much less corrosive than zinc chloride. Effect on paint: zinc chloride cannot be successfully painted over; sodium fluoride does not injure paint. Convenience of shipping: zinc chloride is shipped in 50 per cent. soln. or solid, but the solid form is deliquescent and must be sealed in air-tight containers; sodium fluoride is shipped as dry powder in slack cooperage. Present cost: zinc chloride is about 4*d.* per lb.; sodium fluoride about 7½*d.* per lb.

According to H. G. Denham,[25] the **hydrolysis** of zinc chloride soln.: $ZnCl_2+2H_2O \rightleftharpoons Zn(OH)_2+2HCl$, has not attained equilibrium in 16 days; F. L. Perrot said that the state of equilibrium is rapidly attained. With a mol of $ZnCl_2$ in 75 mols of water, 3·25 per cent. of the zinc chloride is hydrolyzed. W. Bein found that cadmium chloride soln. are slightly hydrolyzed at low temp., and the amount of hydrolysis increases as the temp. rises. J. H. Long found for a mol of cadmium chloride per 1·06 litres at 85°, a hydrolysis of 2·08 per cent., and M. Chanoz for ½*N*-soln., 0·05 per cent. Zinc chloride readily forms basic salts. A large number of basic zinc chlorides, or zinc oxychlorides, have been reported [26] by R. Schindler, R. Bunsen, G. André, R. J. Kane, etc. Writing the mol. ratio in the order $ZnO : ZnCl_2 : H_2O$, the following oxychlorides have been reported: 9 : 1 : 3;

8 : 1 : 10 ; 6 : 1 : 6 ; $5\frac{1}{2}$: 1 : n ; 5 : 1 : 6 ; 5 : 1 : 8 ; 9 : 2 : 12 ; 4 : 1 : 11 ; 4 : 1 : 6 ; 4 : 1 : 0 ; 3 : 1 : x ; 3 : 1 : 5 ; 3 : 1 : 3 ; 5 : 2 : 26 ; 3 : 2 : 11 ; 1 : 3 : 1 ; and 1 : 1 : $1\frac{1}{2}$.

Zinc hydroxide or oxide is soluble in aq. soln. of a zinc salt, and when a conc. soln. is diluted with water, a basic salt is precipitated. According to A. Sordelli, water does not precipitate a basic chloride from conc. soln. of zinc chloride, but **zinc henaoxytetrachloride,** $2ZnCl_2.11ZnO$, is precipitated from a sat. soln. of zinc oxide in one of zinc chloride. Solubility determinations of zinc oxide in aq. soln. of zinc chloride were found by A. Driot to indicate the existence of $ZnCl_2.4ZnO.6H_2O$ and of $ZnCl_2.ZnO.1\frac{1}{2}H_2O$, both of which were isolated. The composition of these two substances does not vary with temp. The first is amorphous and loses $5H_2O$ at 200°, and the latter, which occurs in microscopic crystals, loses one H_2O at 230°, and decomposes at a higher temp. R. Schindler made **zinc enneaoxydichloride,** $ZnCl_2.9ZnO.3H_2O$, by adding water to a syrupy soln. of zinc chloride evaporated until fumes of hydrogen chloride are evolved ; and also by filtering a soln. of zinc chloride treated with ammonia insufficient for complete precipitation. R. J. Kane made it by adding potassium hydroxide to an aq. soln. of zinc chloride until it reacts alkaline. The white powder cannot be completely freed from chlorine by boiling with a soln. of potassium carbonate. It is insoluble in water ; sparingly soluble in aq. ammonia ; and easily dissolved by acids. G. André made **zinc octoxydichloride,** $ZnCl_2.8ZnO.10H_2O$, by treating zinc diammino-chloride, $ZnCl_2.2NH_3.H_2O$, with hot water. The heat of formation is 1·4 cals. R. J. Kane made **zinc hexaoxydichloride,** $ZnCl_2.6ZnO.6H_2O$, by treating zinc monammino-chloride, $Zn(NH_3)Cl_2$, or $Zn(NH_3)_2Cl_2.\frac{1}{2}H_2O$, with water ; and by adding aq. ammonia to a soln. of zinc chloride until the precipitate partially dissolves. The white powder is insoluble in water ; when calcined, it loses water, and a residue is formed from which water extracts zinc chloride, and a higher oxychloride remains. G. André prepared **zinc pentoxydichloride,** $ZnCl_2.5ZnO.8H_2O$, by adding water to a syrupy soln. of zinc chloride. The heat of formation is 2·5 cals. F. L. Perrot made it by pouring 100 c.c. of water at 10° on 5–6 grms. of anhydrous zinc chloride ; and washing the mass free from undecomposed zinc chloride. It is dried in vacuo, and then at 38° over sulphuric acid ; he regarded his preparation as hexahydrate. J. Habermann obtained **zinc enneaoxytetrachloride,** $2ZnCl_2.9ZnO.12H_2O$, as a white insoluble powder, by adding dil. aq. ammonia, with constant stirring, to a boiling conc. soln. of zinc chloride until a precipitate appears. If this compound be washed for a long time, G. André found that **zinc tetraoxydichloride,** $ZnCl_2.4ZnO.11H_2O$, is produced ; the heat of formation is 3·2 cals. If the salt $2ZnCl_2.3ZnO.11H_2O$ is heated with alcohol, $ZnCl_2.4ZnO.6H_2O$ is formed. This salt was also obtained by A. Driot—*vide supra.* R. Schindler made **zinc trioxydichloride,** $ZnCl_2.3ZnO.2H_2O$, by boiling a fairly conc. soln. of zinc chloride and oxide ; by adding to a soln. of zinc chloride insufficient aq. ammonia for complete precipitation, and digesting the precipitate with the mother liquid. The former process gives octahedral crystals, the latter process, a white powder. The product is slightly soluble in water, easily soluble in an aq. soln. of zinc chloride, in dil. acids, in aq. ammonia, and in a soln. of potassium hydroxide. This salt was also made by V. S. M. van der Willigen. A. Werner represented the trihydrate by the structural formula

$$\left[Zn\left(\begin{matrix}HO\\HO\end{matrix}Zn\right)_3\right]Cl_2$$

G. André made hexagonal plates of a pentahydrate by heating a soln. of zinc chloride with zinc oxide ; and by treating a soln. of zinc chloride with insufficient ammonia for complete precipitation. A. Mailhe made the pentahydrate by the action of mercuric oxide on a cold soln. of zinc chloride, and G. André gave for the heat of formation 2·6–3·0 Cals. J. Allan made crystals of **zinc diammino-trioxydichloride,** $ZnCl_2.3ZnO.2NH_3.4H_2O$, by adding alcohol to an ammoniacal soln. of

zinc chloride, and allowing the mixture to stand for some days. When zinc chloride is treated with lead oxide, G. André said that a **zinc lead oxychloride,** $3(ZnCl_2.3ZnO).2(PbCl_2.PbO).14H_2O$, is formed; and copper oxide gives a **zinc cupric oxychloride,** $(ZnCl_2.ZnO.2CuO)(ZnCl_2.3CuO)6H_2O$, but mercuric oxide does not form a double oxychloride. G. André boiled 150 grms. of fused zinc chloride, 40 grms. of zinc oxide, and 400 grms. of water with ammonium chloride and obtained **zinc pentoxytetrachloride,** $5ZnO.2ZnCl_2.26H_2O$. He also reported **zinc trioxytetrachloride,** $3ZnO.2ZnCl_2.11H_2O$, obtained by boiling a soln. of zinc chloride with zinc oxide and cooling the clear soln. A. Driot made **zinc monoxydichloride,** $ZnCl_2.ZnO.1\frac{1}{2}H_2O$, as indicated above. F. Ephraim made **zinc oxyhexachloride,** $3ZnCl_2.ZnO.H_2O$, by the action of a soln. of 2 mols of zinc chloride on a mol of lithium carbonate. The six-sided plates lose water when heated, and then give off vapours of zinc chloride. Water decomposes the salt with the separation of zinc hydroxide. It is soluble in dil. acids. G. André made **zinc dodecammino-oxychloride,** $2ZnCl_2.ZnO.12NH_3.4H_2O$, or $6ZnCl_2.ZnO.12NH_3.4H_2O$, by dissolving anhydrous zinc chloride in conc. ammonia, and evaporating the clear liquid. The heat of formation with liquid water is given as 134·58 Cals. In the absence of a systematic study in the light of the phase rule, apart from chemical analyses, there is little to show which of these salts is a chemical individual, and which a mixture. There is little doubt that several of these oxychlorides are mixtures, and the remarks with respect to the magnesium oxychlorides apply to the zinc and cadmium oxychlorides. R. de Forcrand said that G. André's products are probably addition products of zinc chloride and zinc hydroxide. G. Rousseau obtained zinc oxychlorides by heating a conc. soln. of zinc dioxide with the carbonates of the alkaline earths.

E. Sorel prepared a cement, *Sorel's cement*, by a process analogous to that employed for Sorel's magnesia cement, and it was recommended as a dental cement by G. Feichtinger in 1858; J. F. Persoz employed a soln. of zinc oxide in zinc chloride as a solvent for silk, cotton, but other vegetable fibres are not attacked. The zinc oxychlorides are also used in making paint.

F. Canzoneri, A. de Schulten, etc., have reported a number of **cadmium oxychlorides** with $CdO : CdCl_2 : H_2O$, as 2 : 1 : 0; 1 : 1 : 1; and 1 : 1 : 7. E. Biron, and G. Carrara noted the formation of cadmium oxychlorides during the electrolysis of soln. of cadmium chloride. F. Canzoneri made cadmium dioxydichloride, $2CdO.CdCl_2$, by melting cadmium oxide and chloride, or by heating cadmium itself with an excess of the chloride. The grey powder is insoluble in water, but is slowly decomposed by that liquid into cadmium oxide and chloride. A. de Schulten made cadmium oxydichloride, $CdO.CdCl_2.H_2O$, or $Cd(OH)Cl$, by heating for 1 to 2 days in a sealed tube, a mixture of a soln. of cadmium chloride with calcium carbonate at 200°; E. Tassilly, and J. Habermann, by adding dil. aq. ammonia to a well-stirred soln. of cadmium chloride. The hexagonal prisms have a sp. gr. 4·56 at 15°; at 280°, they lose only one-tenth per cent. of water, the rest is given off at a red heat. The heat of formation given by E. Tassilly is $CdCl_{2aq.}+CdO+H_2O = 2Cd(OH)Cl_{aq.}+10·2$ Cals. A. Mailhe made a heptahydrate, $CdCl_2.CdO.7H_2O$, by adding cadmium oxide to an excess of a soln. of the chloride; and E. Tassilly, a hemihydrate, $CdCl_2.CdO.\frac{1}{2}H_2O$, by the action of cadmium oxide on ammonium chloride.

Several **ammonium zinc oxychlorides** have been reported with $ZnO : ZnCl_2 : NH_4Cl$ as 1 : 2 : 4; 1 : 3 : 5; 1 : 2 : 8; and 1 : 3 : 10. G. André obtained **ammonium zinc oxyoctochloride,** $4NH_4Cl.2ZnCl_2.ZnO$, from the mother liquor remaining after the separation of zinc oxychloride from a hot soln. of zinc oxide, zinc chloride, and ammonium chloride; the next crop of crystals furnished **ammonium zinc oxyhenachloride,** $5NH_4Cl.3ZnCl_2.ZnO$. Both products are decomposed by water. He also reported **ammonium zinc oxyhexadecachloride,** $10NH_4Cl.3ZnCl_2.ZnO$, and **ammonium zinc oxydodecachloride,** $8NH_4Cl.2ZnCl_2ZnO$, with heats of formation respectively of 3·71 and 3·24 Cals. The individuality of these compounds has not been definitely established.

W. Eidmann [27] said that zinc chloride is soluble in *methyl alcohol*, and G. Carrara and L. d'Agostini, and W. Hampe said the same about cadmium chloride, and, added W. Hampe, the soln. is a good electrical conductor. C. A. L. de Bruyn says that at 15·5°, 100 grms. of methyl alcohol dissolve 1·71 grms. of cadmium chloride. Zinc and cadmium chlorides are soluble in *ethyl alcohol*. C. A. L. de Bruyn said that 100 grms. of ethyl alcohol at 15·5° dissolve 1·52 grms. of cadmium chloride; and H. Jahn that unit volume of an alcoholic soln. at 20° contains 0·03129 grm. of $CdCl_2$, and the sp. gr. is 0·83168. T. Graham found the soln. is formed "with great facility, and when filtered has a light amber colour; it may be conc. to a very great extent without injury, and becomes so viscid when cold that it may be inverted without flowing perceptibly." He found that this soln. deposits small crystals of **zinc alcoholo-chloride,** $ZnCl_2.C_2H_5OH$. Some heat is developed during the soln. of zinc chloride in alcohol; S. U. Pickering found 9·767 Cals. per mol of zinc chloride. A. Blümcke measured the sp. and mol. ht. of the alcoholic soln. of zinc chloride; W. Hittorf, G. Vicentini, and C. Cattaneo measured the electrical conductivity of soln. of zinc chloride in ethyl alcohol; G. Coffetti of cadmium chloride in methyl alcohol; and W. Hittorf, the transport numbers of the ions of zinc chloride in ethyl alcohol. E. Rimbach and O. Weber found the addition of levulose lowered the conductivity of alcoholic soln. of cadmium chloride. H. C. Jones, and A. W. Smith estimated a 6·5 per cent. ionization in a $\frac{1}{10}N$-soln. of zinc chloride. S. Arrhenius measured the degree of ionization in methyl, ethyl, and isopropyl alcohol soln. of cadmium chloride, as well as in ether and acetone. In the partition of cadmium chloride between amyl alcohol and water, W. Herz and M. Lewy found the salt is probably polymerized in the amyl alcohol. H. Jahn found the sp. electromagnetic rotation of the plane of polarization of an alcoholic soln. of sp. gr. 0·83168 (20°) to be 1·1856. H. C. Jones and A. Campetti found the alcoholic soln. of zinc or cadmium chloride to be electro-positive towards the aq. soln.; and L. Kahlenberg gave the e.m.f. of the two combinations Zn : $ZnCl_2$ in alcohol, and in water, each against a normal electrode, as 0·910 and 0·195 volt respectively. According to L. Levi-Bianchini, methyl alcohol decomposes cadmium chloride at the critical temp. of the soln.

W. Hampe says that anhydrous zinc chloride is soluble in anhydrous *ether* and cadmium chloride insoluble. R. Lespieau measured the lowering of the f.p. of ethereal soln. of zinc chloride. W. Hampe found that conc. soln. conduct electricity, depositing zinc on the cathode; dil. soln. do not conduct so well. W. Eidmann, and W. H. Krüg and K. P. McElroy, found zinc chloride to be readily soluble in *acetone*, and cadmium chloride is slightly soluble. H. E. Patten found zinc to be deposited from acetone soln. of zinc chloride by a current of 2 volts. A. Naumann, and M. Müller have studied the chemical reactions of zinc chloride in acetone soln.—hydrogen sulphide gives a white turbidity which clears with the further passage of the gas; silver nitrate gives a white precipitate of silver chloride; potassium thiocyanate gives a white precipitate of potassium chloride; and the filtered soln. deposits prismatic crystals of $ZnCl_2.2KCl$; with ammonium thiocyanate, a precipitate of ammonium chloride is formed. According to A. Naumann, zinc and cadmium chlorides are soluble in *ethyl acetate*; and, according to M. Gomberg, the soln. of zinc chloride dissolves zinc. N. Castoro found zinc and cadmium chlorides to be soluble in *urethane*, and he determined the mol. wt. of the dissolved salts from the lowering of the f.p. A. Werner says zinc chloride is soluble in *methyl sulphide*; A. Naumann, in *methylal* and *benzonitrile*, and, according to A. Werner, in other *aromatic nitriles*. A. Werner found zinc chloride to be soluble in *pyridine*; E. Beckmann and W. Gabel, in *quinoline*; L. Kahlenberg measured the electromotive force of soln. of zinc chloride in quinoline, pyridine, and in *aniline*. According to A. T. Lincoln, zinc chloride is readily soluble and a good conductor in *furfurol*, *methyl-propylketone*, *acetophenone*, *ethyl monochloroacetate*, *ethyl acetoacetate*, *ethyl oxalate*, pyridine, and quinoline; the conductivity is feeble in *ethyl cyanoacetate*, *ethyl benzoate*, and *amyl nitrite*; there is no conductivity in *benzyl alcohol*, and *piperidine*; and the salt is insoluble in *salicylaldehyde*, *ethyl nitrate*, and *nitrobenzene*. A. T. Lincoln, also, says that cadmium chloride is insoluble or very sparingly soluble in alcohol, furfurol, acetophenone, ethyl monochloro-acetate, ethyl cyanacetate, ethyl oxalate, ethyl nitrate, amyl nitrite, *o-nitro-toluene*, pyridine, piperidine, and quinoline. G. P. Baxter and M. A. Hines say cadmium chloride is insoluble in *toluene*. J. W. Klever says that zinc chloride is soluble in *glycerol*, and C. Cattaneo measured the conductivity of the soln. Z. Klemensiewicz says zinc chloride is insoluble in *antimony trichloride*.

According to H. Schulze,[28] zinc chloride is readily converted to zinc oxide when it is heated in **oxygen,** or better with potassium chlorate. P. Schutzenberger found that when heated to dull redness in a stream of **hydrogen,** a white deposit of zinc chloride is formed. This is not prevented by first passing the gas through glass wool, and he considers that a volatile *zinc hydrochloride*, ZnHCl, is formed. W. D. Bancroft and H. B. Weiser found that the vapours of zinc and cadmium chlorides are readily reduced when fed into the bunsen flame, and bright mirrors of the metal are deposited on a cold porcelain tube held in the flame. The metal is liable to burn again to the oxide. Zinc chloride gives a blue to bluish-green flame, and cadmium, a yellow flame; both colours are characteristic of the respective metals burning in oxygen.

A. Helfenstein found that molten zinc chloride dissolves metallic zinc—30 grms. of neutral zinc chloride, free from water and hydrogen chloride, dissolved at 700°, 0·0406 grm. of zinc more than at 290°; and R. L. Datta and H. Sen prepared what they regarded as **zincosic chloride,** Zn_3Cl_5, *i.e.* $ZnCl.2ZnCl_2$, by saturating fused zinc chloride with zinc. The bluish-white product is rapidly hydrolyzed by water. *Zinc subchloride* has not been prepared. R. L. Datta and H. Sen's product is probably a soln. of zinc in zinc chloride. According to H. N. Morse and H. C. Jones, when pure anhydrous cadmium chloride is heated in vacuo or in an atm. of nitrogen; the red liquid on cooling freezes to a light grey mass, and when heated again melts to a garnet-red liquid, which decomposes to cadmium chloride and the metal. The product is a powerful reducing agent—it reduces nitric acid to nitrogen oxides, and with dil. acids develops hydrogen. It has, therefore, been suggested that the product contains *cadmium subchloride*, Cd_4Cl_7, or, as H. N. Morse and H. C. Jones suggest, a soln. of *cadmous chloride* in cadmic chloride; but there is a greater probability that the product is a soln. of cadmium in cadmium chloride. According to H. Brandhorst, soln. of **zinc oxide** in molten zinc chloride are good conductors of electricity.

A. Levallois found **lead sulphide** dissolves in molten zinc chloride. On account of its great affinity for **water,** anhydrous zinc chloride is used as a reagent in organic chemistry. Thus, it carbonizes wood, dehydrates alcohols—*e.g.* it forms amylene with amyl alcohol—and it saponifies fats. It forms compounds with ethylenic hydrocarbons, organic bases, etc. When zinc chloride soln. were heated for 10 hrs. in a bomb at 212°, H. W. Fischer [29] found a white amorphous colloid is precipitated. The action of aqua **ammonia** and hydrogen sulphide on soln. of zinc chloride resembles the action on soln. of zinc sulphate (*q.v.*). According to L. Höpfner, soln. of zinc chloride dissolve **zinc sulphite,** and this the more the greater the conc.; lead sulphite is not dissolved. C. J. J. Fox measured the solubility of **sulphur dioxide** in aq. soln. of cadmium chloride. M. C. Schuyten found that **bromine** and **iodine** displace chlorine from aq. soln. of zinc chloride on the water-bath. With **sodium molybdatodiperiodate,** $5Na_2O.12MoO_3.I_2O_5$, C. W. Blomstrand obtained a yellow precipitate. A. Grittner says the soln. of zinc chloride attacks iron—this is no doubt determined by hydrolysis. C. F. Cross and E. J. Bevan, and E. Bronnert investigated the solvent action of zinc chloride soln. on **cellulose;** and A. Leclerc, on **starch.** J. H. Long and H. Ley investigated the effect of zinc and cadmium chloride solutions on the inversion of **sugar.** G. Gore found 100 grms. of dry **silica** dust raised the temp. of 50 c.c. of a 10 per cent. soln. of zinc chloride 0·20°. J. Wagner has studied the influence of cadmium chloride and of ferrous salts on the reaction between hydrochloric acid and potassium permanganate, and J. Brown showed that in this reaction, oxygen is evolved when cadmium chloride is present; if absent, chlorine is evolved. A. A. Noyes found a $\frac{1}{5}N$-soln. of cadmium chloride dissolved as much **lead chloride** as a $\frac{1}{10}N$-soln. of magnesium, manganese, calcium, or zinc chloride.

According to R. Engel,[30] when a current of dry hydrogen chloride at ordinary temp. is passed through a soln. of zinc chloride, and pieces of metallic zinc are frequently added, as the sp. gr. approaches 2·0 (25°), crystals begin to appear

about the gas tube. The soln. is then filtered, cooled to 0°, and evaporated over phosphorus pentoxide. Rhombohedral crystals of **zinc hydrochloride,** $2ZnCl_2.HCl.2H_2O$, are formed ; and if the mother liquid be treated with hydrogen chloride, crystals of $ZnCl_2.HCl.2H_2O$ are formed. J. M. Tschelzoff has studied the progressive decomposition of these two compounds with water. A. Werner regards the one as $H(ZnCl_3).2H_2O$, and the other as $H(Zn_2Cl_5).2H_2O$. M. Berthelot prepared what he regarded as crystals of **cadmium dihydrochloride,** $CdCl_2.2HCl.7H_2O$, by leading a current of hydrogen chloride into a cold sat. hydrochloric acid soln. of cadmium chloride ; and he gave the heat of formation : $CdCl_2+2HCl+7H_2O$ =40·2 Cals. E. Cornec and G. Urbain's study of the f.p. curves of soln. of cadmium chloride in hydrochloric acid indicates the formation of $CdCl_2.HCl.nH_2O$. J. Wagner has studied the viscosity, the lowering of the f.p., and the electrical properties of soln. of cadmium chloride in hydrochloric acid.

According to G. Gore,[31] and E. C. Franklin and C. A. Kraus, zinc and cadmium chlorides are insoluble in liquid ammonia. Zinc chloride forms a number of ammino-compounds when it is exposed under various conditions to the action of ammonia, as was observed by P. Grouvelle in 1821. There is some uncertainty as to the chemical individuality of some of the alleged zinc ammino-compounds. F. Isambert passed ammonia gas over anhydrous zinc chloride, and he found that there was a copious development of heat, and the solid increased about 20 times in vol. The product is **zinc hexammino-chloride,** $ZnCl_2.6NH_3$, and F. Isambert found the dissociation press. rose steadily from 82 to 1722 mm. as the temp. rose from 16·4° to 78·5°. B. Kuriloff, and I. Bouzat, and F. Ephraim, also measured the dissociation press. of this compound. F. Ephraim gave 57·5° for the temp. of decomposition. C. Antoine represented the vap. press., p mm., at $\theta°$, by $\log p=4·9445(2·4391-1000/t)$, where $t=\theta+449$. F. Isambert obtained evidence of the existence of di- and tetra-ammino-chlorides as well as of the hexammino-salt. J. F. Persoz believed that a mol of ammonia is absorbed, and R. J. Kane prepared what he regarded as **zinc monammino-chloride,** $ZnCl_2.NH_3$, by melting either the di- or tetra-ammino-compounds. On cooling, an amber-yellow gummy mass is obtained, which is very slightly crystallized. According to B. Kuriloff, the dissociation press. at 216° is 6·7 mm. R. J. Kane found that the product can be distilled undecomposed at a red heat, and with water, it forms **hydrated zinc tetrammino-chloride,** and zinc oxy-chloride. R. J. Kane, and J. C. G. de Marignac made the last-named compound in talc-like crystals by cooling the soln. obtained by passing ammonia into a hot conc. soln. of zinc chloride until the precipitate first formed has redissolved ; and F. Ephraim says the soln. must be sat. with ammonia gas and cooled in an atm. of ammonia. A. A. Blanchard obtained crystals of the same salt from ammoniacal soln. of zinc chloride. The compound is decomposed by water. P. P. Dehérain says the compound has no combined water. F. Ephraim gave 92° for the temp. of decomposition. According to B. Kuriloff, the dissociation tension at 78° is 402·2 mm. and F. Isambert measured the ammonia press. from 31° to 112·5°, and found it rose steadily from 57 mm. to 1750 mm. **Zinc diammino-chloride,** $ZnCl_2.2NH_3$, was obtained by R. J. Kane, and by J. C. G. de Marignac by evaporating the mother liquor remaining after they had prepared the tetrammino-salt ; R. J. Kane also made it by heating the tetrammino-salt to 149° ; H. Ritthausen, by dissolving zinc in a soln. of ammonium chloride aided by cupric chloride, copper, or silver ; G. André, and H. Thoms prepared this salt by dissolving freshly precipitated zinc oxide in a boiling soln. of ammonium chloride ; and on evaporation crystals of $ZnCl_2.2NH_3.H_2O$ and $ZnCl_2.2NH_3.\frac{2}{3}H_2O$ were obtained ; if ammonia be led into a hot conc. soln. of zinc chloride until the precipitate first formed re-dissolves, G. André obtained from the cooling soln. $ZnCl_2.2NH_3.\frac{1}{4}H_2O$. R. J. Kane assigned to the crystals half a mol of water, $ZnCl_2.2NH_3.\frac{1}{2}H_2O$. B. Kuriloff gives 43·6 mm. for the dissociation press. at 216°, and F. Isambert found a rapid rise from 96 mm. at 222° to 1021 mm. at 297°. F. Ephraim said that the temp. of decomposition is not below 200°. According to F. M. Jäger, the crystals are rhombic bipyramids with axial ratios $a:b:c$

=0·9161 : 1 : 0·9508. When heated it forms the monammino-salt. It is decomposed by water, forming an oxychloride. It can be recrystallized from its soln. in one of ammonium chloride. E. Priwoznik found crystals of this salt were formed in Leclanché's cell: $2NH_4Cl + 2MnO_2 + Zn = ZnCl_2.2NH_3 + Mn_2O_3 + H_2O$, but G. E. Davis says the crystals have the composition $Zn(OH)_2.NH_4Cl$. J. L. Davies made **hydrated zinc pentammino-chloride,** $ZnCl_2.5NH_3.H_2O$, by dissolving zinc chloride gradually in a cold conc. soln. of ammonia, and then passing in ammonia gas. When a large precipitate has formed it is allowed to dissolve by warming the soln. On re-cooling, octahedral crystals are obtained which decompose and deliquesce in air. They are soluble in water. G. André gives the heat of formation (water solid) as 73·24 Cals.

Cadmium chloride also forms a series of ammino-compounds. According to H. Croft, if the anhydrous salt be exposed to ammonia gas, there is a rapid absorption of gas and swelling accompanied by the development of heat. The product is **cadmium hexammino-chloride,** $CdCl_2.6HN_3$. W. R. Lang and A. Rigaut recommended the following procedure:

> Three to four grams of cadmium chloride, rendered anhydrous by heating almost to the point of fusion, were placed in a tube with the neck drawn out, to allow of its being afterwards sealed at the blowpipe, and the whole immersed in solid carbonic anhydride. Dry gaseous ammonia was passed slowly into the tube, when the chloride increased in bulk largely, and, in about 2 hrs., a layer of liquid ammonia had formed on the surface of the solid compound; the tube was sealed and left for 20 hrs. It was found preferable to use the salt in small lumps, as, when in powder, the liquid failed to penetrate through the mass, even on standing for a month. The tube was then cooled to −70° and opened, the temp. cautiously raised to −30° by means of methylic chloride, and the liquid ammonia expelled.

E. Schüler obtained the same compound by passing hydrogen chloride through a cold soln. of cadmium chloride sat. with ammonia. This compound is a crystalline powder, but slightly soluble in cold water; it loses ammonia on exposure to air. and when the smell of ammonia has disappeared, the residue is the diammino-compound $CdCl_2.2NH_3$. The hexammino-salt melts when heated and loses all its ammonia. According to W. R. Lang and A. Rigaut, the dissociation press. rises from 46 mm. at 0° to 931 mm. at 69°; B. Kuriloff makes the dissociation press., 331 mm. at 20°; and W. Biltz makes the dissociation temp. at one atm. press., 306°, and the heat of dissociation $CdCl_2.6NH_3 \rightleftharpoons CdCl_2.4NH_3 + 2NH_3$, 10·69 Cals. G. André prepared what he regarded as *cadmium pentammino-chloride*, $CdCl_2.5NH_3$, in small transparent crystals by passing a current of gaseous ammonia into a soln. of cadmium chloride in 20 per cent. aqua ammonia kept cold at 0°. If the crystals are dried by press. between filter paper they become opaque and lose ammonia. W. R. Lang and A. Rigaut show that G. André's crystals are not $CdCl_2.5NH_3$, but rather $CdCl_2.6NH_3$. G. André found that if the hexammino-salt be warmed it passes into **cadmium tetrammino-chloride,** $CdCl_2.4NH_3$. B. Kuriloff found its dissociation press. at 78° to be 1002 mm., and at 20°, 100·5 mm. W. Biltz says that 34·6° is the dissociation temp. for one atm. press. and the heat of dissociation $CdCl_2.4NH_3 = CdCl_2.2NH_3 + 2NH_3$ is 12·24 Cals. G. André assumes the salt is $CdCl_2.4NH_3.\frac{1}{2}H_2O$, and he believes that by warming the hexa- or tetrammino-compound, *cadmium triammino-chloride*, $CdCl_2.3NH_3.\frac{1}{4}H_2O$, is formed; but the evidence is unsatisfactory, for the decomposition of the tetra- or hexa-ammino-chlorides gives **cadmium diammino-chloride,** $CdCl_2.2NH_3$. H. Croft made this compound by dissolving cadmium chloride in a warm soln. of ammonia, and cooling; the white crystalline powder contained with some cadmium hydroxide, and he therefore preferred to prepare the salt by the spontaneous evaporation of a clear soln. of cadmium chloride in an excess of ammonia. G. André made it by pouring a sat. soln. of cadmium chloride in cooled ammonia, and evaporating off the ammonia by warming. W. Kwasnik made the same salt by passing ammonia into a conc. alcoholic soln. of cadmium chloride. E. Tassilly obtained this compound from the mother liquid remaining when a soln. of cadmium chloride is partially precipitated

by ammonia, but H. Grossmann showed that this gives an impure product. W. R. Lang and A. Rigaut made it by moistening hydrated cadmium chloride with a 20 per cent. soln. of ammonia and drying the mass over lime. The white crystalline powder has no smell. W. R. Lang and A. Rigaut said that this compound is stable at 100° ; begins to decompose at about 210°, and the decomposition is not complete at 360°, the mass melts at 400°. E. Tassilly gave the heat of formation $CdCl_2+2NH_3=CdCl_2.2NH_3$ as 37·24 Cals. W. Biltz gave the heat of dissociation $CdCl_2.2NH_3=CdCl_2.NH_3+NH_3$−18·61 Cals. B. Kuriloff said that the dissociation press. at 216° is 361·1 mm., and W. Biltz that the dissociation temp. for one atm. is 508°. W. Kwasnik obtained **cadmium monoammino-chloride,** $CdCl_2.NH_3$, by the distillation of the diammino-salt. B. Kuriloff gave the dissociation press. at 216° as 4·53 mm. and W. Biltz the dissociation temp. at one atm. press. as 611°, and the heat of dissociation, 22·88 Cals.

T. Curtius and F. Schrader [32] produced **zinc hydrazine-chloride,** $ZnCl_2.2N_2H_4$, by adding hydrazine to zinc chloride in an ammoniacal soln. H. Franzen and O. von Mayer studied the product in some detail. **Cadmium hydrazine-chloride,** $CdCl_2.2N_2H_4$, was also prepared, as well as the hydrochlorides, $ZnCl_2.2(N_2H_4.HCl)$, $ZnCl_2.N_2H_4.HCl$, and $CdCl_2.N_2H_4.HCl$. L. Crismer, and G. Antonoff prepared **zinc hydroxylamine-chloride,** $ZnCl_2.2NH_2OH$, and also **cadmium hydroxylamine-chloride,** $CdCl_2.2NH_2OH$, a compound studied by H. Goldschmidt and K. L. Syngros. R. F. Weinland and F. Schlegelmilch made **zinc iodo-chloride,** $ZnCl_2.2ICl_3.8H_2O$.

S. Grünauer [33] made a rough determination of the m.p. of nine mixtures of zinc and ammonium chloride, and found a V-shaped curve with a eutectic at 175° for a mixture of equi-molar parts of the two salts and for a mixture of $ZnCl_2+3NH_4Cl$, the fusion temp. 335°, and for $11ZnCl_2+NH_4Cl$, 290°. There is no hint of the formation of any compound at these temp.—but as already stated the experiments were not satisfactorily searching. The salt $ZnCl_2.NH_4Cl$ is obtained by the fractional crystallization of a soln. of eq. parts of zinc and ammonium chlorides ; the first crop of crystals is $ZnCl_2.3NH_4Cl$, and later, $ZnCl_2.NH_4Cl$. K. Hachmeister studied the f.p., m.p., and b.p. curves of binary mixtures of ammonium and zinc chlorides, and obtained **ammonium zinc pentachloride,** $NH_4Zn_2Cl_5$, or $2ZnCl_2.NH_4Cl$. This makes four fairly well-defined ammonium zinc chlorides, 2 : 1, 1 : 2, 1 : 3, and 1 : 4. K. Hachmeister's equilibrium diagram is shown in Fig. 31. Where *A* represents the region where molten zinc chloride and the vapour of ammonium chloride are in equilibrium ; *B*, the homogeneous liquid phase ; *C*, crystallized zinc chloride and liquid ; *D*, crystalline double salt and liquid ; *E*, crystalline double salt and liquid ; *F*, crystalline ammonium chloride and melt ; *G*, eutectic mixture of zinc chloride and double salt ; and *H*, eutectic mixture of ammonium chloride and double salt. The regions of existence of the three double salts $ZnCl_2 : NH_4Cl$, 1 : 2, 1 : 3, and 1 : 4, are represented accordingly. P. P. Dehérain said :

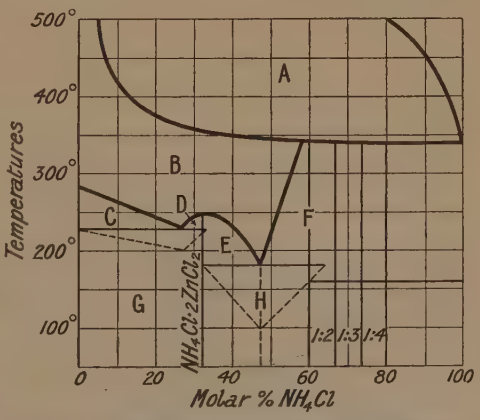

FIG. 31.—Equilibrium Diagram of Mixtures of Zinc and Ammonium Chlorides.

When an ammoniacal soln. of zinc chloride, $2ZnCl.NH_3$, is treated with hydrogen chloride, it deposits fine crystals of a chloro-salt with the formula $2ZnCl.NH_4Cl$, sometimes in hexagonal spangles and sometimes in needle-like crystals terminated by points.

The formulæ used by P. P. Dehérain are in the old notation and correspond respectively with $ZnCl_2.NH_3$ and $ZnCl_2.NH_4Cl$ in the notation of the present day. R. J. Kane stated that on dissolving zinc mono- and tetra-ammino-chlorides in hydrochloric acid, the corresponding double salts are formed, but D. Base has shown the former gives rise to $ZnCl_2.2NH_4Cl$, and the latter to $ZnCl_2.3NH_4Cl$; nor could D. Base obtain different results from J. C. G. de Marignac, only $ZnCl_2.2NH_4Cl$ and $ZnCl_2.3NH_4Cl$ could be obtained by mixing soln. of all proportions of the component salts—zinc and ammonium chlorides. O. Hautz reported the formation of the salt $ZnCl_2.NH_4Cl.2H_2O$ from a mixed soln. of one part of ammonium chloride and two of zinc chloride, but this has not been confirmed by later work. J. I. Pierre prepared $ZnCl_2.2NH_4Cl$ by the evaporation of a mixture of equi-molar proportions of the component salts. J. I. Pierre's work has been confirmed by C. F. Rammelsberg. The crystals separate in thin plates which, according to J. C. G. de Marignac, belong to the rhombic system and have axial ratios $a : b : c = 0{\cdot}7221 : 1 : 0{\cdot}5696$. The sp. gr. is 1·879, according to H. Schiff; 1·71–1·77 (10°), according to C. H. D. Bödeker; and 1·77, according to R. Romanis. R. Schindler obtained clear rectangular prisms of $ZnCl_2.2NH_4Cl.H_2O$, by evaporating a soln. of one part of zinc oxide in conc. hydrochloric acid mixed with one part of ammonium chloride, and, from time to time, replacing the acid which had evaporated. O. Hautz made the same salt in large plates by mixing two eq. of hydrochloric acid with one of zinc carbonate, then adding another eq. of the acid, and saturating the soln. with ammonia. According to O. Hautz and G. Bassayre one part of salt dissolves in one-half or two-thirds its weight of cold water with the absorption of heat, and in 0·28 part of boiling water. L. J. Thénard also made the salt by dissolving zinc hydroxide in a soln. of ammonium chloride.

J. C. G. de Marignac prepared the salt $ZnCl_2.3NH_4Cl$ by evaporating a soln. of about two mols of ammonium chloride with one of zinc chloride. The first crop of crystals is **ammonium zinc pentachloride,** or *ammonium pentachlorozincate*, $ZnCl_2.3NH_4Cl$, and the later crop, **ammonium zinc tetrachloride,** or *ammonium tetrachlorozincate*, $ZnCl_2.2NH_4Cl$. P. A. Meerburg showed that with a soln. of this composition the product must always be a mixture of these two salts. The rhombic crystals have axial ratios $a : b : c = 0{\cdot}7822 : 1 : 0{\cdot}6915$. M. Berthelot and G. André claim to have made crystals of $ZnCl_2.3NH_4Cl.H_2O$. According to R. Kane and P. P. Dehérain, a soln. of zinc tetrammino-chloride, $ZnCl_2.4NH_3$, in hydrochloric acid gives needle-like crystals of $ZnCl_2.4NH_4Cl$, but, as indicated above, D. Base showed that the product is really $ZnCl_2.3NH_4Cl$. M. Berthelot and G. André also claim to have made $ZnCl_2.6NH_4Cl.\frac{2}{3}H_2O$, but without describing the method of preparation. Of the eight ammonium zinc chlorides which have been reported, P. A. Meerburg found only two—$ZnCl_2.2NH_4Cl$ and $ZnCl_2.3NH_4Cl$—were capable of existence in aq. soln. between 0° and 30°, when he applied the phase rule; he concluded in opposition to G. André, and, as already assumed by J. C. G. de Marignac, that if hydrated salts are capable of existence, it must be at low temp., not at ordinary temp. While an application of the phase rule has revealed the existence of many unsuspected compounds, these results emphasize how at the same time, the phase rule promises to eliminate from chemistry many "compounds" which are not really such.

The compositions of soln. in equilibrium with solid phases are indicated in Fig. 32 for systems at 0°, 20°, and 30°. The curves *AB*, *BC*, *CD*, and *DE* give the composition of soln. in equilibrium respectively with NH_4Cl, $ZnCl_2.3NH_4Cl$, $ZnCl_2.2NH_4Cl$, and anhydrous $ZnCl_2$. The point *A* represents the solubility of ammonium chloride, *E* that of anhydrous zinc chloride in water (30°); at *B*, there are the two solid phases NH_4Cl and $ZnCl_2.3NH_4Cl$; at *C*, the two solid phases $ZnCl_2.3NH_4Cl$ and $ZnCl_2.2NH_4Cl$; and at *D*, the two solid phases $ZnCl_2$ and $ZnCl_2.2NH_4Cl$. The isotherm *ABCDE* separates the triangle into two parts—*WABCDE* gives the composition of unsat. soln.; *ABCDEZY*, the composition of soln. which split into one or two solid phases. All points in the sectors *ABY*, *BCN*, *CDM*, and *DEZ* separate into a soln. whose composition is represented by a point respectively on the curves *AB*, *BC*, *CD*, and *DE*, and a solid phase NH_4Cl, $ZnCl_2$, $3NH_4Cl$, $ZnCl_2.2NH_4Cl$, and $ZnCl_2$. Points in the triangles *BYN*, *CMN*, *DMZ* represent the composition of soln. which

split into a soln. represented by the points *B*, *C*, *D* respectively, and two solid phases, $NH_4Cl+ZnCl_2.3NH_4Cl$; $ZnCl_2.3NH_4Cl+ZnCl_2.2NH_4Cl$; and $ZnCl_2+ZnCl_2.2NH_4Cl$. The points *E* for 20° and 0° are not given in the diagram.

G. C. Wittstein,[34] and K. von Hauer found that cadmium oxide, hydroxide, or carbonate dissolved in a soln. of ammonium chloride with the evolution of ammonia, and on evaporation, the soln. furnished crystals with very variable proportions of ammonium and cadmium chlorides. If the soln. be boiled, K. von Hauer found that crystals of **ammonium cadmium hexachloride,** $CdCl_2.4NH_4Cl$, are formed. According to O. Lehmann, a mixed soln. of cadmium and ammonium chlorides gives a crop of mixed crystals with a little cadmium chloride, after which, A. Johnsen found that crystals of $CdCl_2.4NH_4Cl$ are produced, while soln. richer in cadmium chloride give crystals of $CdCl_2.NH_4Cl$. The compound $CdCl_2.2NH_4Cl$ does not appear to exist. H. Croft found that the spontaneous evaporation of a mixed soln. of equimolar parts of cadmium and ammonium chlorides gives needle-like crystals of **ammonium cadmium trichloride,** $CdCl_2.NH_4Cl$, or NH_4CdCl_3, which, according to K. von Hauer, can be dried over sulphuric acid. G. P. Baxter and M. A. Hines purified the product by recrystallization from water. H. Grossmann prepared the same salt from a soln. obtained by boiling cadmium hydroxide with ammonium chloride. E. Rimbach made it by shaking the salt $CdCl_2.4NH_4Cl$, with insufficient water for complete soln. at ordinary temp., the liquid was then separated from the mass of needle-like crystals which were drained on porous tiles, and then dried at 100°. K. von Hauer assumed the crystals had $\frac{1}{2}H_2O$ as water of crystallization, but after heating to 120° a number of times, the crystals are anhydrous. E. Rimbach showed that the crystals belong to the rhombic system, and have axial ratios $a:b:c=0{\cdot}6056:1:0{\cdot}7992$. E. Rimbach also represents the solubility between 2·4° and 105·9° by the expression $S=29{\cdot}88+0{\cdot}2144\theta$, and he found no decomposition within this range of temp. At 16°, 100 grms. of water dissolve 50·26 grms. of salt; at 41·2°, 63·83 grms.; and at 105·9°, 109·33 grms. According to H. Croft, the needle-like crystals of $CdCl_2.NH_4Cl$ gradually pass into rhombohedral prisms, and, according to K. von Hauer, the mother liquor, after the separation of $CdCl_2.NH_4Cl$, furnishes rhombohedral crystals of $CdCl_2.4NH_4Cl$. Both statements, says E. Rimbach, are *unzurverlässig*; but H. L. Wells and P. T. Walden obtained crystals such as K. von Hauer described. The salt $CdCl_2.4NH_4Cl$, or $(NH_4)_4CdCl_6$, was prepared by E. Rimbach by boiling a soln. of 17·8 grms. of cadmium chloride 36·8 grms. of ammonium chloride, and 100 grms. of water, and adding a mixture of $CdCl_2+4NH_4Cl$ until the soln. is sat. Crystals of $CdCl_2.4NH_4Cl$ separate on cooling to 16°. G. André, E. Tassilly, and H. Grossmann made the same salt by the prolonged boiling of cadmium oxide or hydroxide in a soln. of ammonium chloride. According to A. Schrauf, large rhombohedral (ditrigonal) crystals are formed with the axial ratios $a:c=1:1{\cdot}5704$, and $\alpha=108°\ 59'$, and, according to A. Johnsen, isomorphous with the salt $CdCl_2.4KCl$; and sp. gr. 2·01. A. Schrauf gives the indices of refraction as $\omega=1{\cdot}5958$, $\epsilon=1{\cdot}5961$ for the *B*-line; $\omega=1{\cdot}6038$, $\epsilon=1{\cdot}6042$ for the *D*-line; $\omega=1{\cdot}6110$, $\epsilon=1{\cdot}6114$ for the *E*-line; and $\omega=1{\cdot}6414$, $\epsilon=1{\cdot}6418$ for the *H*-line. The crystals are optically positive, and they conduct heat fairly well. E. Rimbach gives the transformation point: $CdCl_2.4NH_4Cl=CdCl_2.NH_4Cl+3NH_4Cl$ at −20°. Very near the cryohydric temp. this salt can be crystallized unchanged from soln. of hydrochloric acid or lithium, calcium, or magnesium chloride.

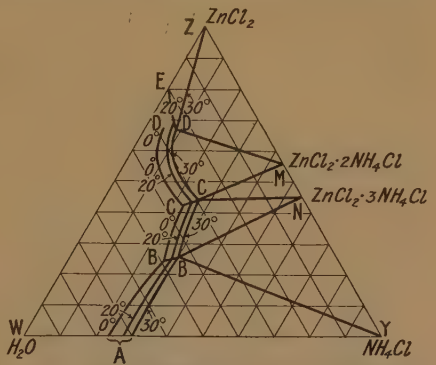

FIG. 32.—Equilibrium Curves of Solutions $ZnCl_2-NH_4Cl-H_2O$.

K. Hachmeister studied the f.p., m.p., and b.p. curves of binary mixtures of cadmium and ammonium chlorides, and he obtained crystals of **ammonium cadmium pentachloride,** $2CdCl_2$, NH_4Cl. This makes three fairly well defined ammonium chlorides, 2 : 1, 1 : 1, and 1 : 4. K. Hachmeister's results are shown in Fig. 33, where *A* represents the region where liquid cadmium chloride is in equilibrium with vap. of ammonium chloride ; *B*, the homogeneous liquid phase ; *C*, equilibrium between crystals of cadmium chloride and liquid ; *D*, equilibrium between crystals of ammonium chloride and liquid ; *E*, eutectic mixture of cadmium and ammonium chlorides ; *F*, crystals of the double salt 1 : 2 and liquid ; *G*, eutectic mixture of cadmium chloride and the double salt 1 : 2 ; *H*, crystals of the double salt 1 : 2 and liquid ; *I*, eutectic mixture of the double salts 1 : 1 and 4 : 1 ; and *K*, eutectic mixture of the double salt 4 : 1 and ammonium chloride.

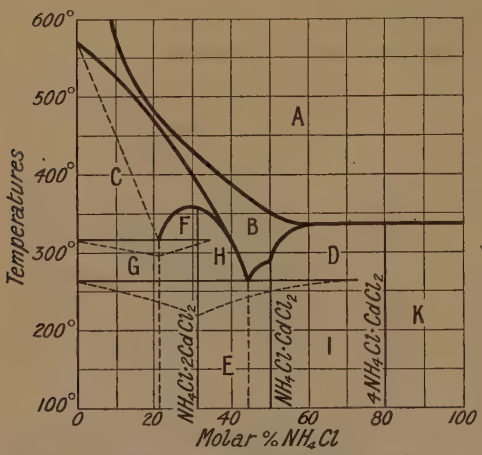

FIG. 33.—Equilibrium Diagram of Mixtures of Cadmium and Ammonium Chlorides.

A. Benrath [35] noted the very small rise in the b.p. of alcohol caused by the addition of zinc and lithium chlorides. F. Ephraim obtained very hygroscopic prisms of **lithium zinc trichloride,** $LiCl.ZnCl_2.3H_2O$, or $LiZnCl_3.3H_2O$, by dissolving a mol of lithium carbonate in an aq. soln. of two mols of zinc chloride and adding hydrochloric acid until all the lithium carbonate was dissolved. The liquid when conc. by evaporation gave crystals of the salt in question. Evaporation of the mother liquid gave an oxychloride. F. Ephraim also obtained hygroscopic prisms of $2LiCl.ZnCl_2.2H_2O$ from a soln. with the calculated amounts of the components. A soln. with six mols of lithium chloride to one of zinc chloride gave on evaporation crystals of lithium chloride and a syrupy liquid which did not crystallize at −12°, but, after standing in a desiccator for six months, gave crystals corresponding with $3LiCl_2.ZnCl_2.10H_2O$. A. Chassevant prepared hygroscopic needle-like crystals of **lithium cadmium trichloride,** $LiCl.CdCl_2.3\frac{1}{2}H_2O$, or $LiCdCl_3.3\frac{1}{2}H_2O$, from a soln. containing $CdCl_2$: LiCl in the proportions 1 : 2. The crystals can be dehydrated at 120°, and they are soluble in alcohol.

F. Ephraim prepared **sodium zinc tetrachloride,** $ZnCl_2.2NaCl.3H_2O$, or $Na_2ZnCl_4.3H_2O$, by evaporating, on a water-bath, a soln. of equi-molar parts of the component salts, or by evaporating over sulphuric acid a soln. containing twice as much zinc chloride. The crystals in the former case are acicular, and, in the latter case, small hexagonal prisms which lose all their water in vacuo, or at 100°. The crystals are decomposed on dilution with water ; they are not very hygroscopic. H. C. Jones and N. Knight have measured the electrical conductivity of aq. soln.

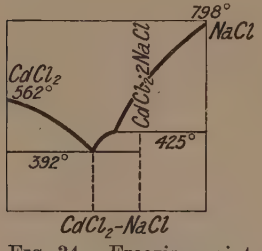

FIG. 34.—Freezing-point Curve of Binary Mixtures of Cadmium and Sodium Chlorides.

H. Brand studied the f.p. curve of binary mixtures of cadmium and sodium chlorides. Only a single compound is formed, **sodium cadmium tetrachloride,** $2NaCl.CdCl_2$, which breaks up at 425° into sodium chloride and liquid. There is a eutectic at 392° with 45 molar per cent. of sodium chloride. H. Croft prepared small crystals of **sodium cadmium tetrachloride,** $2NaCl.CdCl_2.3H_2O$, which, according to K. von Hauer, are stable in air and lose about two-thirds of their water of

crystallization at 100°, and the remainder between 150° and 160°. According to H. Croft, one part of the salt dissolves in 1·4 parts of water at 16°; and, according to K. Sudhaus, 100 mols of water at 19·3° dissolve 3·93 mols of the double salt; 4·29 mols at 29·7°; 4·73 mols at 40·1°; and 5·18 mols at 54·5°. The salt is also soluble in alcohol. According to A. S. Cushman, cadmium sulphide is not precipitated from soln. of the salt by hydrogen sulphide; F. Rüdorff found that the crystals are decomposed by dialysis. K. Sudhaus investigated the equilibrium conditions for the ternary system, $CdCl_2$—$NaCl$—H_2O, at 19·3°, 29·7°, 40·1°, and 54·5°. Soln. in equilibrium with the three solid phases at the temp. indicated, are indicated on the portion of the triangular diagram, Fig. 35. E. Cornec and G. Urbain investigated the lowering of the f.p. of various aq. soln. of cadmium and alkali iodides and obtained results in accord with the known double salts, $CdCl_2.MCl$, where M may be NH_4, K, Na, or H.

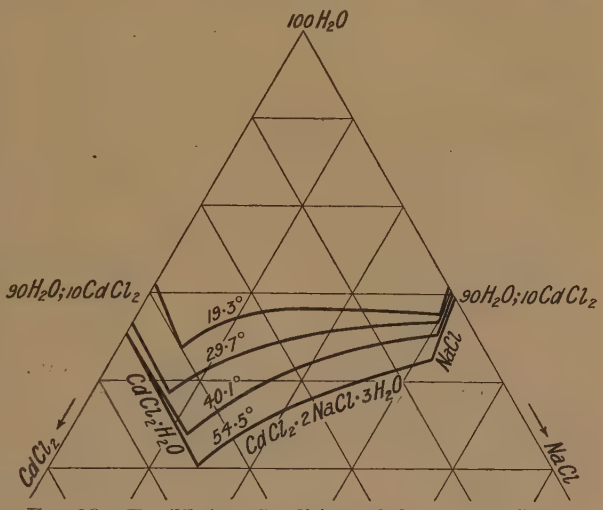

Fig. 35.—Equilibrium Conditions of the Ternary System, $CdCl_2$—$NaCl$—H_2O.

J. I. Pierre, C. F. Rammelsberg, and F. Ephraim obtained **potassium zinc tetrachloride,** $2KCl.ZnCl_2$, or K_2ZnCl_4, from a mixed soln. of the component salts, and J. C. G. de Marignac obtained the same result, whichever component was in excess. A. Neumann made it by shaking an acetone soln. of zinc chloride with potassium chloride, and evaporating off the solvent. H. Schiff gives the sp. gr. 2·297; and the rhombic crystals, according to J. C. G. de Marignac, have the axial ratios $a : b : c = 0·7177 : 1 : 0·5836$, and they are isomorphous with the ammonium salt. H. Steinmetz made observations on the habit of the crystals. J. I. Pierre says they dissolve in their own weight of cold water, and in all proportions in boiling water. The crystals are very deliquescent, and melt at about 200°. H. Kopp gives the sp. ht. as 0·152. H. C. Jones and K. Ota have measured the electrical conductivity of aq. soln. of the salt; C. Sandonnini, the electrical conductivity and sp. gr. of fused mixtures of the two salts; and H. C. Jones and N. Knight, the lowering of the f.p.; and S. Labendzinsky, and C. Immerwahr the potential of the salt soln. against zinc and a normal calomel electrode. R. Schindler, and F. Ephraim also reported $ZnCl_2.2KCl.H_2O$, formed in small prisms by evaporating a soln. of a mol of zinc chloride with five-sixths of a mol of potassium chloride; the mother liquid, F. Ephraim adds, furnishes thick prisms of $KCl.ZnCl_2.2H_2O$ belonging to the monoclinic system.

H. Brand investigated the binary system, KCl—$CdCl_2$, and found two compounds, rhombic crystals of potassium cadmium trichloride, $CdCl_2.KCl$, m.p. 431°, with a maximum on the f.p. curve, Fig. 36; and potassium cadmium hexachloride, $CdCl_2.4KCl$, which breaks up at 460° into KCl and liquid. The two eutectics occur at 382° and 34 molar per cent. KCl, and 390°, with 63 molar per cent. KCl. H. Brand also studied the f.p. curves of ternary mixtures of cadmium, sodium, and potassium chlorides. The compound $CdCl_2.KCl$ does not form solid soln. There are three ternary eutectics, 354°, 370°, and 373°; and six surfaces of primary crystallization.

The presence of cadmium chloride raises the temp. at which solid soln. of potassium and sodium chlorides break up into their components.

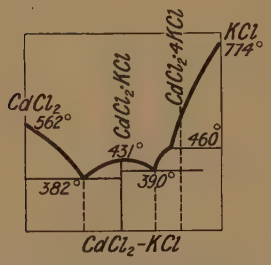

Fig. 36.—Freezing-point Curves of Binary Mixtures of Cadmium and Potassium Chlorides.

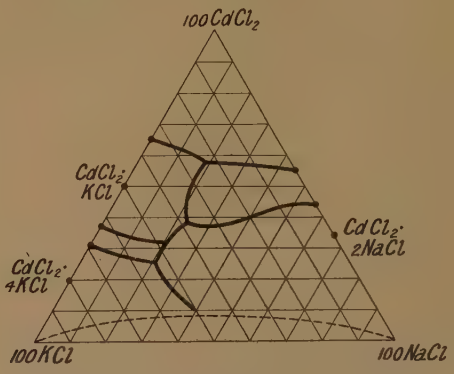

Fig. 37.—Freezing-point Curves of the Ternary System, $CdCl_2$—KCl—NaCl.

F. Bourion and E. Rouyer measured the b.p. of mixed soln. of cadmium and potassium chlorides. K. Sudhaus investigated the equilibrium conditions of the ternary system, $CdCl_2$—KCl—H_2O, at 19·3, 29·7°, 40·1°, and 54·5°. His results are summarized in the portion of the triangular diagram, Fig. 38, where *AB* represents

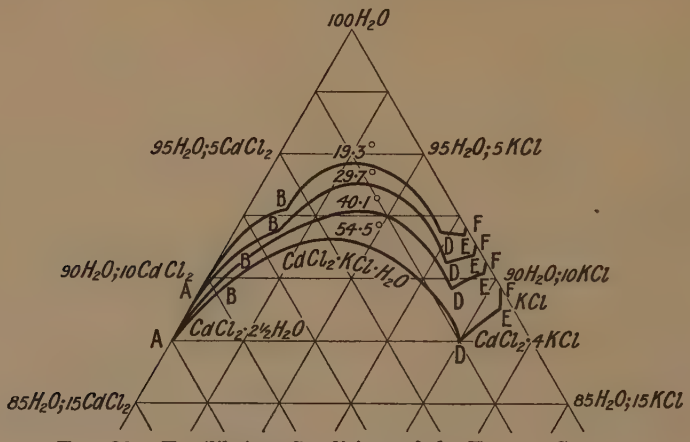

Fig. 38.—Equilibrium Conditions of the Ternary System, $CdCl_2$—KCl—H_2O.

the soln. in equilibrium with the solid phase, $CdCl_2.2\frac{1}{2}H_2O$, *BD*, with $CdCl_2.KCl.H_2O$; *DE*, with $CdCl_2.4KCl$; and *EF*, with KCl. R. Lorenz and co-workers measured the sp. gr. of fused mixtures of potassium and cadmium chlorides. K. von Hauer, and H. Croft prepared long prismatic crystals of **potassium cadmium trichloride,** $KCl.CdCl_2.H_2O$ or $KCdCl_3.H_2O$, by the spontaneous evaporation of soln. of the two salts in the right proportions. According to H. Traube, the crystals are monoclinic, and lose part of their water in dry air, or over sulphuric acid, and all is lost at 100°; the crystals melt at a higher temp. and lose chlorine. The salt is very readily soluble in water without decomposition, and it may be recrystallized from this solvent. E. Rimbach found 100 grms. of water at 15·9° dissolve 36·25 grms. of the salt; at 60·6°, 68·55 grms.; and at 105·9°, 106·91 grms. K. Sudhaus found the solubility to be in mols of $CdCl_2.KCl.H_2O$ per 100 mols of water:

	15·9°	19·3°	29·7°	40·1°	41·5°	54·5°	60·6°
$CdCl_2.KCl.H_2O$	2·53	2·65	3·21	3·72	3·87	4·33	4·79

E. Rimbach prepared crystals of the hemihydrate, and he represents the solubility S between 105° and 2·6° by $S=22·20+0·2901\theta$; and he adds that the increase in solubility with temp. is greater than with the component salts alone. W. Kistiakowsky, H. C. Jones and K. Ota, and H. C. Jones and N. Knight have measured the lowering of the f.p.; and H. C. Jones and K. Ota, and C. F. Lindsay the conductivity of soln. of this salt. According to K. von Hauer, the evaporation of the mother liquid, remaining after the separation of the preceding salt, gives rhombohedral crystals of **potassium cadmium hexachloride,** $4KCl.CdCl_2$. According to E. Rimbach, if the boiling mother liquid prepared from 13·3 grms. of cadmium chloride, 31·9 grms. of potassium chloride, and 100 grms. of water, be sat. with a mixture of $CdCl_2$ and KCl in the molar ratio 1 : 4, and then cooled to 24°, crystals of potassium cadmium hexachloride, analogous with $4NH_4Cl.CdCl_2$ are formed, belonging to the trigonal system, and having the axial ratio. $a:c=1:0·6067$ and $\alpha=109°\ 38'$. According to H. G. F. Schröder, the sp. gr. of the crystals is 2·5; they are stable in air, and when heated, behave like $CdCl_2.KCl$. K. Sudhaus gave for the solubility of the salt, in mols of $CdCl_2.4KCl$ per 100 mols of water:

	19·3°	23·6°	29·7°	40·1°	50·2°	54·5°
$CdCl_2.4KCl$	41·65	45·35	49·05	57·55	68·89	69·91

The decomposition of the salt by water is hindered by the presence of hydrochloric acid; and the chlorides of lithium, calcium, etc. The aq. soln. is stable between −3° and 109°. With soln. containing four litres per mol of cadmium chloride, and two litres per mol of potassium chloride at 17°, R. Varet gives the heat of formation as $(CdCl_2+2KCl)=20$ cals., and $(2CdCl_2+2KCl)=28$ cals. W. Kistiakowsky, and H. C. Jones and N. Knight have measured the lowering of the f.p.; H. C. Jones and K. Ota, and C. F. Lindsay, the electrical conductivity of soln. of the salt; and S. Labendzinsky, and C. Immerwahr, the electrical potential of the salt soln. against cadmium and a normal electrode. According to V. von Lang, there is a feeble positive double refraction, and A. Schrauf gives the indices of refraction $\omega=1·5841$, $\epsilon=1·5842$ for the B-line; $\omega=1·5906$, $\epsilon=1·5907$ for the D-line; $\omega=1·5965$, $\epsilon=1·5966$ for the E-line; and $\omega=1·6208$, $\epsilon=1·6210$ for the H-line. V. von Lang measured the thermal conductivity of the crystals.

R. Godeffroy prepared crystals of **rubidium zinc tetrachloride,** $ZnCl_2.2RbCl$, by the evaporation of a soln. of the component salts, and he also reported a series of **rubidium cadmium tetra- and tri-chlorides,** $CdCl_2.2RbCl$; $CdCl_2.RbCl.\frac{1}{2}H_2O$; but E. Rimbach could verify only $RbCl.CdCl_2$ and $4RbCl.CdCl_2$ analogous with the corresponding ammonium and potassium salts. E. Rimbach made rhombic crystals of $RbCl.CdCl_2$ by evaporating a soln. with the component salts in equi-molar proportions. The axial ratios are $a:b:c=0·5969:1:0·5244$. The salt is stable in water between 0° and 104°, and the solubility at 1·2° is 12·97 per cent.; at 14·5°, 16·8 per cent.; at 41·4°, 25·31 per cent.; at 57·6°, 30·83 per cent.; and at 103·9°, 46·62 per cent.; or the solubility S between 0° and 104° is $S=12·17+0·3279\theta$. The temp. coeff. is greater than is the case with the individual salts. If a boiling soln. of 2·9 grms. cadmium chloride, 32·4 grms. of rubidium chloride, and 100 grms. of water be sat. with a mixture of $CdCl_2$ and RbCl in the molar proportions 1 : 4, and cooled to 14°, it furnishes trigonal crystals isomorphous with the corresponding ammonium and potassium salts. The axial ratio is $a:c=1:0·6323$. The crystals are decomposed by water: $4RbCl.CdCl_2 \rightleftharpoons 3RbCl+RbCdCl_3$; the presence of hydrochloric acid or of lithium, calcium, or other chloride hinders the decomposition. Accordingly, E. Rimbach made the same salt by evaporating a soln. of the component salts with a great excess of rubidium chloride; and from a soln. in hydrochloric acid, sat. with hydrogen chloride at 60°.

H. L. Wells and G. F. Campbell prepared colourless monoclinic prisms of **cæsium zinc pentachloride,** $3CsCl.ZnCl_2$, by adding zinc chloride to a conc. soln. of cæsium chloride all in the required proportions. If a larger proportion of zinc chloride is used, colourless plates of $2CsCl.ZnCl_2$ are formed. The latter salt forms under a

wide range of conditions, and it can be crystallized unchanged from water. R. Godeffroy prepared this salt in a similar manner in 1875, and he remarks on its extremely large solubility in water and dil. hydrochloric acid. H. L. Wells and P. T. Walden obtained small rectangular plates of **cæsium cadmium tetrachloride,** $2CsCl.CdCl_2$, or Cs_2CdCl_4, produced as a precipitate when a soln. of cadmium chloride is added to a conc. soln. of cæsium chloride; and with a soln. of 50 grms. of cæsium chloride and 3 grms. of cadmium chloride, this salt continued to be formed until the proportion of cadmium chloride was increased to 18 grms. when $CdCl_2.CsCl$ was formed as a white crystalline powder. R. Godeffroy made the salt $CdCl_2.2CsCl$ from a conc. hydrochloric acid soln. of the component salts. The salt $CdCl_2.2CsCl$ is very sparingly soluble in soln. of cæsium chloride, a fact which explains why no cadmium salt analogous to the 3 : 1 cæsium zinc chloride could be obtained. If the attempt be made to crystallize $CdCl_2.2CsCl$ from water, crystals of $CsCl.CdCl_2$, or $CsCdCl_3$, are obtained. This salt can be recrystallized from water. It is sparingly soluble in water, and especially so in conc. soln. of cadmium chloride.

O. Menge [36] studied the f.p. curves of binary mixtures of calcium chloride with zinc and cadmium chlorides; in the former case, the curve gives signs of a eutectic very close to the m.p. of zinc chloride; and, in the latter case, a continuous series of mixed crystals is formed although the two salts are not isomorphous. The f.p. curve here shows a minimum which C. Sandonnini placed at 545°. K. von Hauer, J. Grailich, and C. F. Rammelsberg have prepared crystals of **calcium cadmium hexachloride,** $CaCl_2.2CdCl_2.7H_2O$, by concentrating a mixed soln. of the component salts in the molar proportions $CaCl_2 : CdCl_2 = 3 : 4$. If the proportions are 1 : 2 or 1 : 3 the same salt crystallizes out at first, but is later followed by $Ca_2CdCl_6.12H_2O$, or $2CaCl_2.CdCl_2.12H_2O$. Both salts are very hygroscopic. The crystals of $CaCl_2.2CdCl_2.7H_2O$ are monoclinic with axial ratios $a : b : c = 1{\cdot}8728 : 1 : 1{\cdot}8085$, and $\beta = 105° 44'$. At 100°, the salt loses a little water, but the whole of the water is expelled only at a red heat; it melts at a higher temp. and some cadmium chloride is volatilized. With soln. containing a mol of each salt in four litres of water at 17°, R. Varet gives the heat of formation $CaCl_2 + 2CdCl_2 = 30$ cals. The anhydrous salt dissolves in water with the evolution of heat, the hydrated salt with the absorption of heat; similar remarks apply to $2CaCl_2.CdCl_2,12H_2O$. The salt $2CaCl_2.CdCl_2.12H_2O$ melts at 100° in its water of crystallization, and loses about half its combined water at 100°, and the other half at 150°–155°. It melts at a higher temp. with partial decomposition. The salt effloresces in vacuo over sulphuric acid. C. Sandonnini found evidence of **strontium zinc tetrachloride,** $SrCl_2.ZnCl_2$, on the f.p. curve of mixtures of zinc and strontium chlorides. The compound decomposed on melting. J. Grailich prepared **strontium cadmium hexachloride,** $SrCl_2.2CdCl_2.7H_2O$, by crystallization from soln. with one or two mols of cadmium chloride per mol of strontium chloride. The monoclinic crystals over sulphuric acid or calcium chloride, lose about two-sevenths of their combined water at 100°; three-sevenths at 125°–130°; five-sevenths at 170°; and all at about 180°. The salt melts at a higher temp., and some cadmium chloride is volatilized. According to W. Knight, the sp. gr. of the salt at 24° is 2·718. It is very soluble in water. H. C. Jones and N. Knight measured the lowering of the f.p. and the electrical conductivity of aq. soln., and W. Kistiakowsky, the electrode potential. C. Sandonnini found a V-shaped curve for mixtures of strontium chloride—melting at 872°—and cadmium chloride—melting at 568°—the minimum at 500° corresponded with about 54 molar per cent. of $CdCl_2$. He also found that mixtures of zinc and barium chlorides furnished a f.p. curve showing the existence of **barium zinc tetrachloride,** $BaCl_2.ZnCl_2$, with the temp. of formation 470°. O. Ruff and W. Plato made observations on the m.p. of mixtures of barium and cadmium chlorides. There is a eutectic at 475° and 65 molar per cent. of cadmium chloride and a bend in the curve at about 560° and 90 molar per cent. of the cadmium salt. G. Warner prepared small deliquescent needle-like crystals of tetrahydrated barium zinc tetrachloride, $BaCl_2.ZnCl_2.4H_2O$, of sp. gr. 2·845 (24°), by cooling a conc. soln.

of the two salts. K. von Hauer evaporated a soln. containing barium and cadmium chlorides in the mol. proportions 1 : 1, and obtained, first crystals of barium chloride, and later those of tetrahydrated **barium cadmium tetrachloride,** $BaCdCl_4.4H_2O$, or $BaCl_2.CdCl_2.4H_2O$; when the molar proportions are 1 : 2, the double salt $BaCdCl_4.4H_2O$ first crystallizes out, and then follows $BaCd_2Cl_6.5H_2O$, or $BaCl_2.2CdCl_2.5H_2O$; and when the proportions are 1 : 3, the last-named salt alone crystallizes from the soln. According to K. von Hauer, the salt $BaCl_2.2CdCl_2.5H_2O$ loses over two-fifths of its combined water very slowly at 100°, another two-fifths about 160°, and the remainder at a higher temp. At a higher temp. the salt melts, and loses some cadmium chloride by volatilization. E. Rimbach found 100 grms. of water dissolve 83·82 grms. of salt at 22·6°; 96·62 grms. at 41·3°; 104·25 grms. at 59·9°; and 165–166 grms. at 107·2°; and the solubility S at $\theta°$ between 22·6° and 107°, is $S=40·80+0·1988\theta$. According to F. Rüdorff, the component salts diffuse at different rates in aq. soln. The salt $BaCl_2.CdCl_2.4H_2O$ forms triclinic crystals with axial ratios $a:b:c=0·8560:1:0·5067$, and $\alpha=90°\ 51'$, $\beta=106°\ 21'$, $\gamma=89°\ 12'$. W. Knight gives the sp. gr. 2·952 (24°). H. Töpsöe gives 2·968; mol. vol. 78·0. At 100°, it loses over half its combined water, and the remainder at 160°. According to E. Rimbach, 100 grms. of water at 22·5° dissolve 72·06 grms. of salt; at 41·4°, 88·01 grms.; at 53·4°, 101·21 grms.; at 97·8°, 163·5 grms.; and at 109·2°, 188·27 grms.; and the solubility S at $\theta°$ between 22·5° and 109° is $S=35·78+0·2678\theta$. The solubility with each salt has a higher temp. coeff. than either component alone. This salt crystallizes unchanged from its aq. soln., but the component salts diffuse in aq. soln. at different rates. According to R. Varet, the heat of admixture of soln. with a mol of each component in four litres of water at 17° is $CdCl_2+BaCl_2=20$ cals.; $2CdCl_2+BaCl_2=32$ cals.

G. Hermann found cuprous and zinc chlorides form a eutectic, m.p. 243°, with 90 per cent. zinc chloride. Solid soln. are formed at both ends of the series. E. W. Prevost found a deposit on the brass binding screws of a Leclanché cell with the composition of *copper zinc triamminotetrachloride*, $Cu_2Zn_2(NH_3)_3Cl_4$, but there is nothing to show that this is a chemical individual, Cuprous and cadmium chlorides were found by G. Hermann to form a continuous series of solid soln. having a f.p. with a minimum at 410° and 20 per cent. cadmium chloride. A thermal effect is observed at a lower temp. reaching a maximum at 350° and 30 per cent. cadmium chloride. This indicates the formation of **cuprous cadmium hexachloride,** $4CuCl.CdCl_2$. This compound is greyish-blue, and its formation from the solid soln. is promoted by light. K. von Hauer also prepared a series of salts $M_2CdCl_6.12H_2O$, where M denotes magnesium, manganese, cobalt, or nickel; he made a **copper cadmium tetrachloride,** $CuCdCl_4.4H_2O$, by the evaporation of an equi-molar soln. ot the two salts. In aq. soln. of all these salts the properties of the component salts can be recognized, showing that the complexes are more or less resolved into their constituents in aq. soln. O. Menge studied the f.p. curves of binary mixtures of magnesium chloride with zinc and cadmium chlorides. Magnesium and cadmium chlorides are isomorphous and form a continuous series of mixed crystals; with the mixture of zinc and magnesium chlorides, there are signs of a eutectic very close to the m.p. of zinc chloride. G. Warner prepared rhombic hygroscopic prisms of **magnesium zinc tetrachloride,** $MgCl_2.ZnCl_2.6H_2O$, analogous with the barium salt. According to J. Grailich, and C. F. Rammelsberg **magnesium cadmium hexachloride,** $MgCl_2.2CdCl_2.12H_2O$ or $MgCd_2Cl_6.12H_2O$, can be obtained by evaporating a soln. of equimolar proportions or 2 : 1 parts of cadmium and magnesium chlorides; it forms rhombic crystals with axial ratios $a:b:c=0·9130:1:0·3039$. It loses much water in vacuo or over sulphuric acid; and over half its combined water at 100°, with stronger heating the residue melts and loses hydrogen chloride. The salt may be crystallized unchanged from water. E. Rimbach found 100 grms. of water dissolve 83·86 grms. of salt at 2·4°; 98·77 grms. at 20·8°; 115 grms. at 45·5°; and 189·59 at 121·8, and the solubility S at $\theta°$ between 2·4° and 121·8° is $S=45·98+0·16505\theta$; the temp. coeff. is greater than for either of the component salts. The crystals

have a positive double refraction. The refractive indices are $\omega=1{\cdot}5485$, $\epsilon=1{\cdot}6099$ for violet light; $\omega=1{\cdot}5400$, $\epsilon=1{\cdot}5901$ for bluish-green light; $\omega=1{\cdot}5331$, $\epsilon=1{\cdot}5769$ for yellow light; and $\omega=1{\cdot}5268$, $\epsilon=1{\cdot}5728$ for red light. The salt $2MgCl_2.CdCl_2.12H_2O$ or $Mg_2CdCl_6.12H_2O$ is formed by evaporating a soln. of two mols of magnesium chloride and one of cadmium chloride. K. von Hauer says that the presence of free hydrochloric acid hinders the crystallization of both magnesium cadmium chlorides. $MgCd_2Cl_6.12H_2O$ loses very little water—one per cent.—at 100°.

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§ 13. Zinc and Cadmium Bromides

According to C. Mentzel,[1] bromine occurs in the cadmiferous zinc ores of Silesia, and hence it has been inferred, without proof, that zinc bromide occurs in nature. A. J. Balard prepared zinc bromide, $ZnBr_2$, by dissolving zinc in hydrobromic acid ; hydrogen was simultaneously developed. The evaporated liquid crystallizes with difficulty. According to R. Dietz, the sat. neutral soln. at 38° to 40° gives octahedral crystals of zinc bromide. On account of hydrolysis, some oxide is formed. C. Löwig sublimed the zinc bromide from the residue. C. P. Baxter, M. A. Hines, and H. L. Frevert made cadmium bromide by dissolving cadmium in bromine water acidified with hydrobromic acid to prevent the formation of basic salts. The soln. was heated on a water-bath to drive off every trace of free bromine ; filtered ; and crystallized. The crystals were dried over potassium hydroxide in vacuo. W. L. Hardin prepared cadmium bromide in a similar manner, and the crystals were dried and sublimed in a stream of dry carbon dioxide while heated in a hard glass combustion tube. A. J. Balard noted that bromine water slowly dissolves zinc oxide, forming zinc bromide and bromate, but the liquid does not bleach vegetable colours. J. B. Berthemot prepared cadmium bromide by boiling cadmium and bromine water ; he also passed bromine vap. over heated zinc when colourless fused zinc bromide is formed. He also noticed that cadmium in the cold does not react very well with bromine, but when heated in a stream of bromine vap. a cloud of cadmium bromide is formed. T. W. Richards and E. F. Rogers also obtained highly pure zinc bromide by dissolving purified zinc oxide in purified hydrobromic acid, and the resulting crystals were sublimed and finally heated in a stream of hydrogen bromide and nitrogen. O. W. Huntington also dissolved purified cadmium carbonate in purified hydrobromic acid, and evaporated the soln. to dryness ; he heated the mass to 200° ; and then sublimed the cadmium bromide in a stream of dry carbon

dioxide in a porcelain tube. C. D. Ragland also says that cadmium bromide is prepared more conveniently by dissolving cadmium oxide in bromine water than by passing the vapour of bromine over heated cadmium. T. W. Richards and E. F. Rogers prepared highly purified zinc bromide by treating purified zinc with purified bromine in an atm. of dry carbon dioxide.

About 40 grms. of purified zinc were treated with an excess of purified bromine in a Jena glass flask which was cooled during the reaction. The red soln. was filtered in a glass funnel through asbestos, and the excess of bromine, together with any trace of iodine which might be present, was driven off by leaving the flask in a very much inclined position on a steam-bath for some time. The dil. colourless soln. was evaporated to a small bulk, and the greater part fractionally crystallized by cooling to zero. To sublime the zinc bromide, a glass adapter for conducting the current of carbon dioxide was fitted to the lower part of a platinum retort. The substance to be sublimed was contained in a small platinum crucible fitted with a wire handle, by which it could be easily raised, lowered, or removed. The adapter was so arranged that the current of gas came as closely as possible in contact with the crucible, and so that any zinc bromide which might condense in a liquid form upon the glass, and thus run the risk of taking alkali from it, must return to the crucible and be re-distilled. The sectional drawing will give a clearer idea of the arrangement (Fig. 39). Two powerful Bunsen burners supplied heat from below, impinging upon a porcelain dish which fitted closely to the bottom of the retort and protected the platinum. The gases from the flame were diverted by a large diaphragm of asbestos board. By means of this arrangement it is possible to sublime about half a grm. of zinc bromide an hour; the crystals are exceedingly beautiful, and give every evidence of great purity. Instead of being sublimed, some of the pure salt was distilled in a current of carbon dioxide. For this purpose a medium-sized tube of the hardest glass was drawn out so as to serve as a small retort, and this was encased in a larger hard glass tube, from which it was separated by several pieces of platinum foil. A platinum boat, into which was directed the drawn-out and turned-over point of the inner tube, served as the receiver. Here, again, a diagram must assist the explanation (Fig. 40). The zinc bromide thus distilled possessed a peculiarly brilliant white lustre.

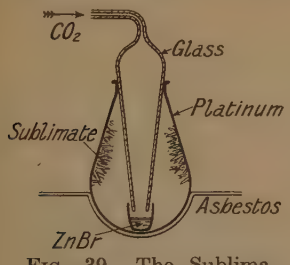

Fig. 39.—The Sublimation of Zinc Bromide.

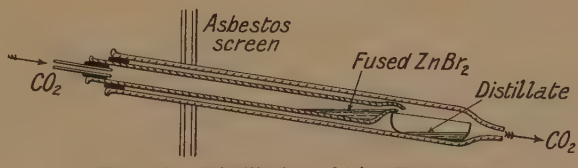

Fig. 40.—Distillation of Zinc Bromide.

W. Ortloff [2] states that zinc bromide forms rhombic crystals with axial ratios $a:b:c=0{\cdot}924:1:1{\cdot}264$. The molten mass of fused zinc or cadmium bromide crystallizes on cooling. Cadmium bromide, on sublimation, gives white plates with a mother-of-pearl lustre.

C. H. D. Bödeker [3] gives the **specific gravity** of zinc bromide as 3·643 (10°); T. W. Richards and E. F. Rogers, 4·219 (4°); and C. H. D. Bödeker found for cadmium bromide, 4·712–4·910 (14°); F. W. Clarke, 4·794 (19·9°); and G. P. Baxter and M. A. Hines, 5·192 at 25°, water unity at 4°. W. Biltz gave 52·43 for the mol. vol. of cadmium bromide.. A. J. Rabinowitsch measured the sp. gr. and **viscosities** of soln. of zinc and cadmium bromides. According to S. Motylowsky,[4] the drop weights W of zinc and cadmium bromides at their m.p. are respectively 44 and 87, where the **surface tension**, σ, is $\sigma=0{\cdot}076W$. C. A. Valson found that for soln. with 0, 5, 10, and 35 grms. of $CdBr_2$ in 100 c.c. of water, the capillary height in a tube of $\frac{1}{2}$ mm. diameter was $h=60{\cdot}6$, 58·2, 56·0, and 49·0 mm.

The reported numbers for the **melting point** of zinc bromide vary from the 390° of L. Graetz [5] to the 394° ± 2·5° of T. Carnelley. For the m.p. of cadmium bromide, T. Carnelley gave 571°; O. H. Weber, about 580°; L. Graetz, 585°; and R. Nacken 567°. R. Nacken observed no breaks in the heating or cooling curves of cadmium

bromide. K. Mönkemeyer observed with cadmium bromide a **transformation point** between 379° and 384°; G. Hermann said at 394°. R. Nacken obtained a U-shaped curve, Fig. 41, for the f.p. of mixtures of cadmium chloride—melting at 563°—and of cadmium bromide—melting at 567°—with a minimum at 551° when 60 per cent. of $CdCl_2$ is present. R. Dietz also obtained mixed crystals of $CdCl_2.CdBr_2.5H_2O$. According to T. Carnelley and W. C. Williams, the **boiling point** of zinc bromide lies between 695° and 699°; V. Meyer and F. Freyer give 642·0 to 652·4°; V. von Czepinsky, 670° to 680°; W. Hampe, 697°; the b.p. of cadmium bromide is 806° to 812°, according to T. Carnelley and W. C. Williams, and 963°, according to O. H. Weber. The **vapour density** of cadmium bromide found by V. and C. Meyer is 9·25 between 914° and 923°—the calculated value for $CdBr_2$ is 9·40. According to G. Tammann,[6] the mol. wt. of cadmium bromide, calculated from the lowering of the vap. press. of aq. soln., is abnormal.

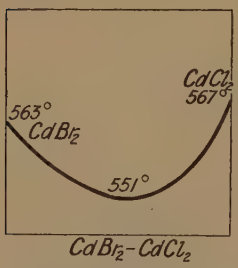

FIG. 41.—Fusion Curve of Mixtures of Cadmium Bromide and Chloride.

Determinations of the **molecular weight** of zinc and cadmium bromides in organic solvents have been made. E. Beckmann found from the effect of zinc bromide on the b.p. of quinoline, a mol. wt. of 222; the calculated value for $ZnBr_2$ is 235·3; and from the b.p. cadmium bromide, 271; when the calculated value is 272·3. A. Werner found that by increasing the conc. of a soln. of cadmium bromide in piperidine from 2·06 to 9·47 per cent., the mol. wt. rose from 280 to 329.

According to W. Hallwachs,[7] the coeff. of **cubical expansion** of a 35·84 per cent. soln. of cadmium bromide is 0·000046. According to C. Helmreich, the **specific heat** of cadmium bromide from 0° to 30° is 0·06561; from 0° to 50°, 0·06690; and from 0° to 70°, 0·06809. C. Helmreich gives for the sp. ht. C and mol. ht. C' of 16·13 and 41·98 per cent. soln. of cadmium bromide from 0°–30°, respectively C=0·84123, C'=24·60, and C=0·60533, C'=21·64; and from 0°–70°, C=0·83357, C'=5·99; and C=0·60204, C'=17·99. O. H. Weber's value for the heat of fusion of cadmium bromide is 5·0 to 5·2 Cals. G. G. Person gives for the **latent heat of fusion** of a mol of zinc bromide 1·83 Cals.; V. von Czepinsky, 1·91 to 1·98 Cals.

The **heat of formation** of zinc bromide is 75·93 Cals., according to J. Thomsen;[8] 85·13 Cals., according to R. de Forcrand; and 87·2 Cals., according to M. Berthelot. M. Herschkowitsch gives for the soln. of cadmium in bromine, 77·46 Cals.; J. Thomsen, 76·3; W. Nernst, 77·3. R. Lorenz and M. G. Fox give for the change of free energy in the formation of molten cadmium bromide, at $\theta°$, between 580° and 720°, W=1·045–0·000742(θ—580), and by substituting this value of W in J. W. Gibbs and H. von Helmholtz's formula, Qp=23046n($W-TdW/dT$), the thermal value of the reaction can be computed. V. von Czepinsky gives for the heat of formation of zinc bromide, calculated from the free and bound energy, 76·544 Cals. at 360°; 80·119 Cals. at 390°; 89·597 Cals. at 460°; 96·944 Cals. at 530°; and 141·124 Cals. at 460°. J. Thomsen found the **heat of solution** of a mol of $ZnBr_2$ in 400 mols of water, to be 17·03 Cals.; and for $CdBr_2$, 0·76 Cal.

The **solubility** of zinc bromide in water has been determined by A. Étard,[9] R. Dietz, etc. R. Dietz's data show the percentage composition or the number of grams of $ZnBr_2$ in 100 grms. of soln.:

	−15°	−10°	−8°	0°	15°	30°	35°	40°	80°	100°
$ZnBr_2$	77·1	78·45	79·06	79·55	80·7	84·08	85·4	85·57	86·57	87·05
Solid phases	$ZnBr_2.3H_2O$			⇌	$ZnBr_2.2H_2O$		⇌	$ZnBr_2$		

At the transition points −8°, B, Fig. 42, and 35°, D, Fig. 42, there are two solid phases. The unstable regions BC and DE have been realized. At the higher temp. the hydrate with the smaller proportion of water of crystallization becomes the more stable. H. Lescœur obtained indications of **monohydrated zinc bromide,**

$ZnBr_2.H_2O$, from his measurements of the vap. press. R. Dietz obtained rhombic plates of **dihydrated zinc bromide,** $ZnBr_2.2H_2O$, by cooling an 86 per cent. soln. of neutral zinc bromide to 0°. The hydrate melts at 37° to a clear fluid. R. Dietz obtained prismatic crystals of **trihydrated zinc bromide,** $ZnBr_2.3H_2O$, by cooling an 80 per cent. neutral soln. of zinc bromide to —25°; and E. Lubarsky obtained it by seeding with crystals of trihydrated zinc chloride. The crystals melt at —5°, according to R. Dietz, or at —2° to —3°, according to E. Lubarsky, below which "it is possible another hydrate is formed." Both salts are very deliquescent, and their solubility and range of stability are indicated in Fig. 42.

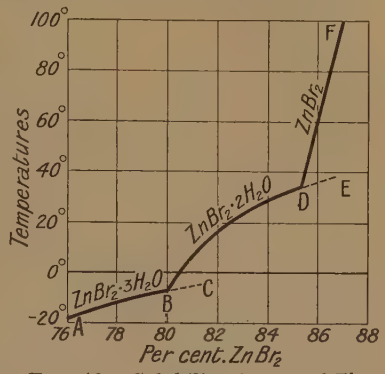

FIG. 42.—Solubility Curves of Zinc Bromide.

R. Dietz, and A. Étard have also partially explored the solubility curves of cadmium bromide—the latter at temp. above 100°, the former below 100°:

	0°	18°	30°	36°	60°	100°	155°	215°	245°
$CdBr_2$ . .	37·92	48·90	56·90	60·40	61·10	61·63	63·7	69·9	71·5
Solid phases .	$CdBr_2.4H_2O$			$\rightleftharpoons$	$CdBr_2.H_2O$				

At the transition point at 36° there are the two solid phases, $CdBr_2.4H_2O$ and $CdBr_2.H_2O$. The unstable $CdBr_2.H_2O$ at 35° with 60·3 per cent. of $CdBr_2$ has been isolated. According to R. Dietz, cadmium bromide forms mono- and tetrahydrated salts. H. Lescœur's vap. press. measurements confirm the existence of the **monohydrated cadmium bromide,** $CdBr_2.H_2O$. Its range of stability and solubility are indicated in the preceding table, when the transition point is near 36°; below this temp., **tetrahydrated cadmium bromide,** $CdBr_2.4H_2O$, is the stable phase. H. Lescœur has studied the vap. press. curve; J. Thomsen found the heat of formation $CdBr_2+4H_2O=77·73$ Cals., and the heat of soln. in 600 mols of water, —7·3 Cals. J. M. Eder reports that one part of the salt dissolves in 0·94 part of water, 3·4 parts of absolute alcohol, in 250 parts of ether (sp. gr. 0·729), and in 16 parts of alcoholic ether.

The **specific gravity** of aq. soln. of zinc bromide has been determined by P. Kremers;[10] and of cadmium bromide by P. Kremers, C. A. Valson, O. Grotrian, F. J. Wershoven, and many others. P. Kremers gives for the sp. gr. of soln. with w grms. of $CdBr_2$ per 100 grms. of water at 19·5°:

w . . .	20·6	42·6	91·4	112·7	150·3	211·1	224·7	318·3
Sp. gr. . .	1·1715	1·3270	1·6101	1·7190	1·8797	2·1095	2·1441	2·3914

The following is a selection from O. Grotrian's and F. J. Wershoven's data for cadmium bromide at 18°:

Per cent. $CdBr_2$	0·0324	0·506	0·013	5·07	10·10	20·11	29·95	42·99
Sp. gr. . .	0·9990	1·0031	1·0075	1·0437	1·0916	1·2004	1·3288	1·5464

P. Kremers has also calculated the increase in volume which occurs during the dissolution of the salts, and also the effect of variations of temp. on the vol. of the soln. With 19·9, 67·5, and 189·2 mols of $ZnBr_2$ per 100 parts of water (vol. of water at 19·5° unity), the respective vol. at 0° are 0·99419, 0·98980, and 0·98840; and at 100°, 1·05011, 1·05640, and 1·05456. Similarly for cadmium bromide, for n=24·3, 44·5, and 68·1 the respective vol. at 0° are 0·99426, 0·99226, 1·00000; and at 100°, 1·04665, 1·04942, and 1·05157. These numbers show that the coeff. of expansion of soln. of these salts increases with increasing conc., and with a falling temp. The lowering of the **vapour pressures** of soln. of 0·5 and 4·0 mols of cadmium

bromide in a kgrm. of water at 100°, are respectively 8·6 and 80 mm., and H. C. Jones and V. J. Chambers' values[11] for the lowering of the f.p. of soln. of the same salt show that the degree of ionization falls from 0·93 to 0·36 as the conc. of the soln. increase from 0·00125 to 0·1124 mols $CdBr_2$ per litre; and that with conc. soln. the ionization is not the simple process symbolized $CdBr_2 \rightleftharpoons Cd^{\cdot\cdot} + 2Br'$, for complex ions are probably present.

The **indices of refraction** of zinc bromide soln. have been measured by P. Kremers[12] at 15° for soln. of sp. gr. 1·3371, 1·7190, and 2·1095 at 19·5° (water at that temp. unity), and the respective values are 1·3881, 1·4446, and 1·5002; and likewise for soln. of cadmium chloride of sp. gr. 1·3310 and 1·5951 (19·5°) the respective indices of refraction are 1·3814 (14°) and 1·4199 (16°). C. Bender gives for a 4*N*-soln. of cadmium bromide at 15°, $\mu(H_\alpha)=1{\cdot}39574$ (19·7°); $\mu(D)=1{\cdot}39835$ (20·2°); $\mu(H_\beta)=1{\cdot}40484$ (19·9°); and $\mu(H_\gamma)=1{\cdot}40996$ (20°). Values have also been reported by H. Jahn, W. Hallwachs, and M. le Blanc and P. Rohland. The sp. **electromagnetic rotation** of the plane of polarization of soln. of cadmium bromide of sp. gr. 1·1628 to 1·3312 (20°) is 1·3044. Analogous results by J. Forchheimer showed that the mol. rotation of cadmium bromide is independent of the conc. and of the degree of ionization of the soln. According to J. A. Wilkinson, cadmium bromide gives a yellowish-white fluorescence, a faint **phosphorescence,** and a weak **thermoluminescence.** C. Sheard and C. S. Morris found that the **emission spectrum** of zinc bromide has an absorption band between 5550 and 5150. E. J. Evans studied the **absorption spectrum** of cadmium bromide vap.

According to F. Braun,[13] anhydrous solid zinc bromide does not **conduct electricity** electrolytically; W. Hampe says that when solid it is a non-conductor, but when fused a good conductor; and V. von Czepinsky said that the fused anhydrous salt is a better conductor than the fused hydrated salt. L. Graetz's values for the conductivity K (mercury unity) are:

	460°	440°	420°	400°	390°	380°	360°	340°	320°
$K\times10^8$ . . .	1000	820	650	504	430	365	250	160	59

Similarly for cadmium bromide:

	620°	600°	590°	585°	580°	570°	560°	530°	510°
$K\times10^3$ . . .	302	288	283	280	235	120	50	7	2·8

There is therefore no abrupt break with zinc bromide in passing from the molten to the solid state; and there is a very faint break with cadmium bromide. The polarization during the electrolysis of fused zinc chloride with rise of temp. falls the more the nearer the b.p., a phenomenon which V. von Czepinsky attributes to the possible depolarizing action of the anode gases diffusing to the cathode more rapidly the higher the temp. According to C. C. Garrard, the decomposition potential of the molten salt is 1·21 volts at 504° in an atm. of carbon dioxide. O. H. Weber gives the e.m.f. of the cell Cd | $CdBr_2$ | Br at a temp. θ between 610° and 780° as $1{\cdot}1319-0{\cdot}000486(\theta-610)$ volts; and V. von Czepinsky, for the cell Zn | $ZnBr_2$ | $PbBr_2$ | Pb, 0·2286 volt at 434°, and 0·1418 volt at 673°. G. C. Schmidt and W. Hechler said that the vap. is also a good conductor, and A. E. Garrett and R. S. Willows, that the molten salt appears to ionize the surrounding atm. J. H. Long's values for the eq. **conductivities** of soln. with a mol of $\frac{1}{2}ZnBr_2$ per litre, and O. Grotrian and F. J. Wershoven's values for $\frac{1}{2}CdBr_2$ per litre at 18°, are:

N- . .	0·0001	0·002	0·01	0·05	0·1	0·5	1·0	4·0	10
$\lambda ZnBr_2$ . .	110	105	98	87	82	65	55	23	7·3
$\lambda CdBr_2$ . .	—	92	65·6	40·1	31	18·3	15·4	7·9	—

G. Jäger's values for the eq. conductivity of zinc bromide soln. and O. Grotrian's for cadmium bromide soln. show a rise to a maximum as the conc. increases, and this is followed by a rapid fall in the conductivity. Cadmium bromide in dil. soln. is almost as strongly ionized as cadmium chloride, and the **degree of ionization**

rapidly falls as the conc. increases. H. C. Jones and co-workers found the mol. conductivity μ and the percentage degree of ionization, α, of soln. containing a mol of cadmium bromide in v litres to be :

v	4	8	32	128	512	2048
$\mu_{0°}$	28·63	37·80	57·78	79·77	101·37	121·23
$\mu_{65°}$	96·4	128·5	202·3	286·4	369·1	436·0
$\alpha_{0°}$	23·1	30·5	46·7	64·4	81·9	97·9
$\alpha_{65°}$	22·1	29·5	46·4	65·7	84·6	100·0

A. J. Rabinowitsch measured the anomalous ionization—*i.e.* the decreased eq. conductivity with dilution of zinc and cadmium bromides. W. Hallwachs obtained analogous results, and C. Immerwahr found that the conc. of the ions is very sensitive to additions of potassium bromide. G. Kümmell's values for the **transport numbers** of the anions of zinc bromide vary from 0·584 to 0·607, in soln. with respectively 0·00272 and 0·0103 mol of $\frac{1}{2}ZnBr_2$ per litre. G. Kümmell also found 0·584 for soln. with 0·010 to 0·0026 mol of $\frac{1}{2}CdBr_2$ per litre. For conc. soln. the evidence, as with the corresponding chlorides, points to the formation of complex anions in conc. soln. V. Gordon found that the transport number of the anions in a conc. soln.—29 per cent.—of $CdCl_2$, varies with temp. θ=8°, anion, 0·894 ; 40°, 1·040 ; and at 75°, 0·970 ; the phenomena here are also explained by the formation of complexes. O. Grotrian, F. J. Wershoven, and C. Cattaneo have measured the temp. coeff. of the conductivity of soln. of cadmium bromide ; C. J. J. Fox has measured the conductivity of aq. soln. of cadmium bromide sat. with sulphur dioxide. A. Gockel has measured the change in the electromotive force of Zn | $ZnBr_2$ and of Cd | $CdBr_2$ with variations of temp. According to S. Meyer, the **magnetic susceptibility** of cadmium bromide in powder form referred to mass units is $-0·30\times10^{-6}$.

Soln. of zinc and cadmium bromides are hydrolytically decomposed by water. G. André [14] reported **zinc hexoxydibromide,** $ZnBr_2.6ZnO.35H_2O$, to be formed by the action of cold water on the tetroxydibromide ; **zinc pentoxydibromide,** $ZnBr_2.5ZnO.6H_2O$, by heating in a sealed tube at 200° a mixture of zinc oxide and bromide ; **zinc tetroxydibromide,** $ZnBr_2.4ZnO.10H_2O$, by heating 100 grms. of zinc bromide with 30 grms. of zinc oxide, and adding a conc. soln. of ammonium bromide until the oxide is dissolved ; he also obtained a tridecahydrate, $ZnBr_2.4ZnO.13H_2O$, by heating a conc. soln. of zinc oxide in zinc bromide, and an enneadecahydrate, $ZnBr_2.4ZnO.19H_2O$, by adding aq. ammonia to a soln. of zinc bromide in amount insufficient for complete precipitation. G. André has also reported a **zinc diammino-trioxybromide,** $3ZnO.ZnBr_2.2NH_3.5H_2O$, by heating in a sealed tube tridecahydrated zinc tetroxydibromide with water at 200°. A. de Schulten made plate-like crystals of a basic cadmium bromide, or **cadmium oxydibromide,** $CdO.CdBr_2.H_2O$, that is, Cd(OH)Br, by heating a soln. of cadmium bromide one or two days with marble in a sealed tube at 200° ; E. Tassilly made the same salt by treating a dil. soln. of cadmium bromide with dil. aqua ammonia. The product has a sp. gr. 4·87 (15°), and heat of soln. 14·35 Cals. It is decomposed by water. Small crystals of the trihydrate, $CdO.CdBr_2.3H_2O$, were made by E. Tassilly by treating a conc. soln. of cadmium bromide with cadmium oxide in a sealed tube at 200°. The crystals act on polarized light ; they are decomposed by water, and more rapidly by alkali lye ; and they are readily soluble in acids. A. Mailhe also reported a heptahydrate, $ZnO.ZnBr_2.7H_2O$, by adding mercuric oxide to an excess of a soln. of zinc bromide.

According to W. Hampe,[15] and J. B. Berthemot, zinc bromide dissolves copiously in anhydrous *alcohol ;* and, according to J. M. Eder, 100 grms. of a sat. soln. of tetrahydrated cadmium bromide in absolute alcohol at 15° contain 20·93 grms. of $CdBr_2$. H. Jahn says the sp. gr. of a soln. of 0·27097 or 0·16088 grm. of cadmium bromide in unit vol. of alcohol is 1·0464 or 0·94361 (20°) respectively ; and the refractive index of a soln. of sp. gr. 1·0461 (20°) is μ_α=1·3950 ; μ_D=1·3970 ; and μ_β=1·4027. H. Jahn found the sp. electromagnetic rotation of the plane of polarization of alcoholic soln. of cadmium bromide of sp. gr. 1·0464 to 0·94361 (20°)

to be on the average 1·3784. C. Helmreich measured the sp. ht., and S. Arrhenius the electrical conductivity and the degree of ionization of alcoholic soln. of cadmium bromide; and C. Cattaneo gives $\mu=14$ as the mol. conductivity at 18° of a 0·001*N*-soln.

W. Hampe says zinc bromide is soluble in anhydrous *ether* and the soln. is electrically conducting. J. Nicklès prepared an unstable compound of ether with zinc bromide which fumed in air. J. M. Eder says 100 grms. of a sat. soln. of tetrahydrated cadmium bromide in absolute ether contain 0·4 grm. of $CdBr_2$ at 15°. W. Hampe says zinc bromide is insoluble in *carbon disulphide*; and E. Beckmann, that it is soluble in *quinoline*. According to P. Dutoit and E. Aston, the mol. conductivity is $\mu=16·2$ for a soln. of a mol of cadmium bromide in 384 litres of *propionitrile*. Cadmium bromide, say W. H. Krug and K. P. MacElroy, is soluble in *acetone*, and, according to A. Naumann, 100 grms. of absolute acetone dissolve 1·559 grms. of cadmium bromide, or 64·5 grms. of acetone dissolve a gram of the salt at 18°—ammonia precipitates $CdBr_2.2NH_3$; hydrogen sulphide, yellow CdS; chlorine, $CdCl_2$; etc. According to J. H. Mathews, cadmium bromide is insoluble in *allyl mustard oil*. Zinc and cadmium bromides also form numerous compounds with *phenylhydrazine* and other organic bases.

According to A. Potilitzin,[16] **oxygen** attacks zinc or cadmium bromide at a red heat, forming a mixture of oxide and bromide. According to A. Potilitzin, and M. Berthelot, the bromides are easily reduced when heated in a stream of **hydrogen** in a glass tube—with cadmium bromide the metal forms an annular deposit with a bright metallic lustre. J. B. Berthemot found zinc bromide to be decomposed by **nitric acid,** but, according to V. Thomas, it is not attacked by **nitrogen peroxide.** With **mercuric oxide,** A. Mailhe obtained **zinc oxydibromide,** $ZnO.HgBr_2.8H_2O$. H. N. Morse and H. C. Jones obtained a product **cadmium subbromide,** Cd_4Br_7, by heating anhydrous cadmium bromide with an excess of metallic **cadmium** in vacuo, or in an atm. of nitrogen. The remarks with respect to cadmium subchloride are applicable here. M. Herschkowitsch found that the soln. of cadmium in an excess of **bromide** gave a larger heat of soln. than corresponded with J. Thomsen's data; and M. Wildermann showed that a mol of cadmium bromide, in soln., unites with nearly a mol of bromine, furnishing **cadmium tetrabromide,** $CdBr_4$; and there is evidence of the formation of the still higher polybromide, $CdBr_6$. M. Berthelot prepared a crystalline **cadmium hydrobromide,** $CdBr_2.2HBr,7H_2O$, analogous to the corresponding chlorine compound. E. Cornec and G. Urbain also found evidence of the existence of $CdBr_2.2HBr.nH_2O$ on their f.p. curves of soln. of the mixed components. M. Adams found that cadmium bromide unites with *hydroxylamine*, to form a white crystalline precipitate of **cadmium hydroxylamino-bromide,** $CdBr_2(NH_2OH)_2$, when an alcoholic soln. of cadmium bromide is treated with free hydroxylamine. The salt is readily soluble in hot water, and the soln. quickly deposits a basic salt; it is readily soluble in dil. acids; and insoluble in alcohol and ether. H. Franzen and O. von Mayer prepared compounds of zinc and cadmium bromides with **hydrazine,** namely, **zinc hydrazinebromide**, $ZnBr_2.2N_2H_4$, and **cadmium hydrazinebromide,** $CdBr_2.2N_2H_4$.

According to G. Gore,[17] and F. C. Franklin and C. A. Kraus, zinc bromide is very slightly soluble and cadmium bromide is insoluble in liquid ammonia. C. F. Rammelsberg made octahedral crystals of **zinc diammino-bromide,** $ZnBr_2.2NH_3$, by saturating a conc. aq. soln. of zinc bromide with ammonia, and concentrating by evaporation. The crystals melt when heated and lose their ammonia; they are decomposed by water into zinc oxide and a soln. of ammonium bromide free from zinc. G. André says the crystals have one mol of water of crystallization. F. Ephraim also prepared this salt. G. André claims to have prepared $3ZnBr_2.6NH_3.H_2O$ by cooling a soln. of zinc hydroxide in a boiling 33 per cent. soln. of ammonium bromide. Crystals can be obtained by heating the product with water in a sealed tube at 200°. He also claims to have made $3ZnBr_2.8NH_3.2H_2O$ by evaporating a soln. of zinc bromide in cold ammonia; and also $3ZnBr_2.10NH_3.H_2O$ by concentrating the soln. obtained by leading ammonia gas through a soln. of zinc bromide until the precipitate first formed re-dissolves. There is nothing to show

which of these products are compounds and which mixtures—all are decomposed by water.

C. F. Rammelsberg made **cadmium diammino-bromide,** $CdBr_2.2NH_3$, by a process analogous to that employed for the zinc salt. H. Croft also made octahedral crystals of this salt by cooling an ammoniacal soln. of zinc bromide ; and by adding ammonia to an acetone soln. of zinc bromide ; H. Grossmann made it by boiling a supersat. soln. of cadmium hydroxide in a conc. soln. of ammonium bromide ; and E. Tassilly found this salt is present in the mother liquid remaining after the preparation of zinc oxybromide by his process. E. Tassilly says the heat of formation is $CdBr_2+2NH_3=35{\cdot}2$ Cals. E. Tassilly also made crystals of **cadmium triammino-bromide,** $CdBr_2.3NH_3$, by passing a stream of ammonia gas into an ammoniacal soln. of cadmium bromide ; and C. F. Rammelsberg obtained a voluminous white powder of **cadmium tetrammino-bromide,** $CdBr_2.4NH_3$, by exposing dry cadmium bromide to ammonia gas. H. Croft says that under these conditions 4 to 6 mols of ammonia are taken up by one mol of cadmium bromide. The salt loses its ammonia when heated, and decomposes in water. F. Ephraim found the decomposition temp. of **zinc tetrammino-bromide** to be 143°, and of **zinc hexammino-bromide,** 62°. He also prepared **cadmium hexammino-bromide,** $[Cd(NH_3)_6]Br_2$. **Zinc pentammino-bromide** was made by G. André by leading ammonia into a soln. of zinc bromide in well-cooled aqua ammonia and warming the mixture until the precipitate re-dissolved. When re-cooled, crystals of this salt were obtained which decomposed in air giving off ammonia gas. This was possibly the incompletely ammoniated hexammina-salt.

F. Ephraim [18] prepared a hydrated **ammonium zinc tribromide,** $NH_4Br.ZnBr_2.H_2O$, by evaporating a soln. of the two components in the mol. proportion 1 : 1, until crystallization begins. On cooling small glistening plates separate. When dried on a porous tile, and kept 12 hrs. over calcium chloride, analyses correspond approximately with $NH_4Br.ZnBr_2.3H_2O$, but there is a doubt if the crystals were adequately dried. C. F. Rammelsberg made deliquescent crystals of $2NH_4Br.ZnBr_2$, or $2NH_4Br.ZnBr_2.H_2O$, by evaporating a soln. of the component salts over sulphuric acid. According to C. H. D. Bödeker, the sp. gr. is 2·625. H. C. Jones and N. Knight, and F. Ephraim report the formation of monoclinic crystals of $3NH_4Br.ZnBr_2.H_2O$ by evaporating a soln. of zinc bromide with equi-molar proportions of ammonium bromide. H. L. Maxwell studied the dissociation of the salt in aq. soln. by the diffusion process.

J. M. Eder [19] obtained crystals of **ammonium cadmium tribromide,** $NH_4Br.CdBr_2$, from a soln. of the component salts ; and E. Tassilly, and H. Grossmann by the action of cadmium oxide on ammonium bromide. E. Rimbach says the crystals are anhydrous ; and J. M. Eder, that they are not decomposed by water between 0° and 110° ; and that one part of the salt dissolves in 0·73 part of water at 15° ; in 5·3 parts of alcohol of sp. gr. 0·794 ; in 280 parts of ether, sp. gr. 0·729 ; and in 24 parts of ethereal alcohol. E. Rimbach and A. Grewe gave the solubility at 1° as 53·82 per cent. ; at 14·8°, 58·01 per cent. ; at 52·2°, 65·32 per cent. ; and at 110·1°, 75·83 per cent., or, the solubility S at $\theta°$ between 1° and 110° is $S=54{\cdot}47+0{\cdot}197\theta$. K. von Hauer obtained crystals of $CdBr_2.4NH_4Br$, from the mother liquid remaining after the separation of $NH_4Br.ZnBr_2$; E. Tassilly, and H. Grossmann by boiling cadmium hydroxide or carbonate with a soln. of ammonium bromide ; and E. Rimbach, by crystallization from a soln. containing 6·85 per cent. NH_4, 14·94 Cd, and 51·48 of bromine. E. Rimbach says that the crystals are trigonal and feebly double refracting with the axial ratio $a:c=1:0{\cdot}6269$. J. M. Eder says that one part of the salt dissolves in 1·4 parts of water at 15°, and that the salt is decomposed by alcohol and ether. According to E. Rimbach, however, the salt is decomposed by cold water, but not if the temp. be 160°, under which condition the salt may be crystallized.

F. Ephraim [20] obtained hygroscopic crystals of **sodium zinc tribromide,** $NaBr.ZnBr_2.H_2O$, and of $2NaBr.ZnBr_2.5H_2O$, by the conc. of a soln. with the mol.

proportions in the former case of NaBr : ZnBr=3 : 4, and the latter case 2 : 1. When heated they are decomposed. H. Croft, and J. M. Eder reported the formation of the complex salts, and J. M. Eder says one part of the salt dissolves in 1·04 parts of water at 15° ; in 3·7 parts of alcohol of specific gravity 0·794 ; and in 190 parts of ether of sp. gr. 0·729. H. C. Jones and N. Knight say $2NaBr_2.3CdBr_2.6H_2O$ exists in conc. soln., and is decomposed by dilution; they determined the electrical conductivity of the soln., but they could not make J. M. Eder's salt, $4NaBr.CdCl_2$. F. Ephraim prepared **potassium zinc tribromide,** $KBr.ZnBr_2.2H_2O$ and $2KBr.ZnBr_2.2H_2O$, from soln. with the mol. proportions $KBr : ZnBr_2=1 : 1$ in the former case, and 2 : 1 in the latter. The crystals of the former are hygroscopic, the latter not so. E. Cornec and G. Urbain measured the lowering of the f.p. of mixed soln. of alkali and cadmium bromides and obtained results in harmony with the composition of the known double salts, $CdBr_2.2MBr$, where M represents NH_4, K, Na, or H. H. L. Maxwell studied the dissociation of **sodium cadmium bromide** in aq. soln. by the diffusion process. K. von Hauer made crystals of **potassium cadmium tribromide,** $KBr.CdBr_2.H_2O$, by evaporating a soln. of equimolecular proportions of the component salts ; the mother liquid gave crystals of $4KBr.CdBr_2$. The former crystals are rhombic, the latter are isomorphous with the rhombohedral crystals of the chlorine compound. The axial ratios of the former are $a : b : c=0·4592 : 1 : ?$; the crystals are stable in air, and, according to H. Croft, very soluble in water ; according to J. M. Eder, one part of the salt at 15° dissolves in 0·79 part of water; according to E. Rimbach, water at 0·4°, 15·8°, 50°, and 112·5° dissolves respectively 53·75, 58·68, 68·25, and 78·11 per cent. of the salt, or the solubility S at $\theta°$ between 0·4° and 112·5° is $S=55·108+0·218\theta$. $KBr.NH_4Br.H_2O$. It is not decomposed by water between 0·4° and 112·5°, but is decomposed by alcohol or ether. H. C. Jones and N. Knight, and C. Immerwahr have measured the electrical conductivity of soln. of $KBr.CdBr_2.H_2O$. According to J. M. Eder, the salt $4KBr.CdBr_2$ is very deliquescent, and dissolves in 1·4 parts of water at 15°, but, according to E. Rimbach, it is decomposed by water into potassium and cadmium bromides. The effect of the presence of hydrochloric acid, lithium potassium, and calcium chlorides is to hinder the decomposition of the salt by water at 16°. R. G. van Name and W. G. Brown obtained evidence of the formation of potassium cadmium tetrabromide, $2KBr.CdBr_2$, in their study of the equilibrium of soln. of the component salts. E. Rimbach prepared **rubidium cadmium tri- and hexa-bromides,** $RbBr.CdBr_2$ and $4RbBr.CdBr_2$, by evaporating a soln. of the component salts. The solubility S of the former salt at $\theta°$ between 0° and 107° is $S=35·34+0·393\theta$, and of the latter between 0° and 115°, $S=50·88+0·2637\theta$. H. L. Wells and G. F. Campbell prepared the **cæsium zinc penta- and tetra-bromides,** $3CsBr.ZnBr_2$ and $2CsBr.ZnBr_2$, by a process analogous with that employed for the corresponding chlorides ; and H. L. Wells and P. T. Walden prepared **cæsium cadmium penta-, tetra-, and tri-bromides,** $3CsBr.CdBr_2$; $2CsBr.CdBr_2$; and $CsBr.CdBr_2$. The two latter are analogous with the corresponding chlorides, but the chloride eq. to $3CsBr.CdBr_2$ has not been made. Cs_3CdBr_5 is obtained in rectangular plates from 120 c.c. of a soln. with 80 grms. cæsium bromide and 4·5 grms. of cadmium bromide ; and Cs_2CdBr_4, in slender needles from 120 c.c. of a soln. containing 52 grms. of cæsium bromide and 3 grms. of cadmium bromide. Both salts on recrystallization from water furnish $CsCdBr_3$, which is also formed from soln. of the component salts mixed in widely varying proportions. The compound $CsBr.CdBr_2$ is dimorphous—cubic when the cæsium bromide is in excess, and in prisms when the cadmium bromide is in excess.

G. Hermann found mixtures of cadmium and cuprous bromides form solid soln. up to 66 per cent. $CdBr_2$, at which there is a eutectic at 420°. Cuprous bromide undergoes a transformation at 394°, and **cuprous cadmium tribromide,** $CuBr.CdBr_2$, is formed in the solid state. K. von Hauer reported the formation of large colourless crystals of **barium cadmium tetrabromide,** $BaBr_2.CdBr_2.H_2O$, isomorphous with the corresponding chloride, by the spontaneous evaporation of soln. of equal

mol. proportions of the two salts. The existence of the double salt in conc. soln. was confirmed by H. C. Jones and N. Knight, who give the formula $BaBr_2.CdBr_2.4H_2O$ for the crystals obtained when the cadmium bromide is in excess. H. C. Jones and N. Knight measured the conductivity. The crystals are double refracting, and, according to A. Murmann and L. Rotter, isomorphous with the corresponding chloride. The sp. gr. is 3·665, according to F. W. Clarke, and 3·687, according to H. Topsöe.

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§ 14. Zinc and Cadmium Iodides

According to C. Mentzel,[1] iodine occurs in the cadmiferous zinc ores of Silesia, and hence it has been inferred, without proof, that zinc iodide occurs in nature. According to J. L. Gay Lussac, iodine unites readily with zinc with the development of a small proportion of heat, forming a readily fusible mass which when heated sublimes, forming four-sided needle-like crystals. The aq. soln. of zinc iodide was made by J. B. Berthemot by bringing together zinc, iodine, and water until the soln. is decolorized. F. Bodroux illustrated the reaction as a lecture experiment by dropping water on a mixture of zinc dust and iodine. The reaction is quite violent. Zinc iodide is also made by dissolving zinc or zinc oxide in hydriodic acid. The evaporation of the aq. soln. over 0° furnishes octahedral crystals of the

anhydrous salt. A. Stromeyer made cadmium iodide either by the action of iodine on heated cadmium, or the mutual action of iodine, cadmium, and water; F. W. Clarke and E. A. Kebler heated eq. quantities of iodine and cadmium in a sealed tube exhausted of air; and A. Vogel made it by evaporating to dryness a soln. of 20 parts of potassium iodide, and 15 parts of cadmium sulphate. The mass was extracted with absolute alcohol, and the alcoholic soln. of cadmium iodide was allowed to crystallize. C. D. Ragland also made this salt by dissolving cadmium or cadmium oxide in hydriodic acid.

According to J. B. Berthemot,[2] and C. F. Rammelsberg, anhydrous zinc iodide forms octahedral crystals belonging to the cubic system; measurements of the crystals of cadmium iodide by J. Grailich, and A. E. Nordenskjöld show that they belong to the hexagonal system and have the axial ratio $a:c=1:0{\cdot}8599$; but R. M. Bozorth's **X-radiograms** correspond with a trigonal not hexagonal structure. The shortest distance between the centres of the iodine and cadmium atoms is 3·00 A.; and between the iodine atoms, 4·21 A. A. G. Duboin prepared mixed crystals of mercuric iodide with cadmium and zinc iodides, without determining their form. A. des Cloizeaux also showed the crystals have a strong negative double refraction. According to J. W. Retgers, cadmium iodide is closely related crystallographically with lead iodide. E. Cohen and A. L. T. Mösveld examined the crystallization of supersat. aq. soln. of cadmium iodide and found that the velocity may be slow owing to the presence of a third substance—possibly cadmium hydroxide, a product of hydrolysis. W. Ackroyd drew attention to the change in colour of the warm iodides with increasing mol. wt. in passing along the series: Magnesium iodide (white), zinc iodide (white), cadmium iodide (white), and mercuric iodide (red). H. C. Jones and C. G. Carroll say that when heated for a long time on an air-bath, cadmium iodide acquires a red colour, which on introducing a trace of water becomes reddish-white. W. Hampe also states that molten cadmium iodide is dark brown; the colour becomes paler on solidification, and on cooling becomes white. W. Hampe says melted zinc iodide is yellow.

The **specific gravity** of anhydrous zinc iodide, according to C. H. D. Bödeker,[3] is 4·696 at 10° and 4·666 at 14·2°; F. W. Clarke and E. A. Kebler gave 4·666. The sp. gr. of the so-called α-variety of cadmium iodide by F. W. Clarke vary from 5·543 to 5·729 (10·5° to 20°); H. B. Fullerton gives 5·9857 (12°) and 5·9738 (13·5°), and for the β-variety 4·596 to 4·688. C. H. D. Bödeker gives 4·596 (10°); F. W. Clarke and E. A. Kebler, 5·644; and J. F. Snell, 5·644. If cadmium iodide be crystallized from its soln. in hydriodic acid the product has a lower sp. gr. than normal cadmium iodide. The marked difference in the sp. gr. has led F. W. Clarke to the assumption that there are two allotropic forms called respectively α- and β-varieties. The normal or α-salt with the higher sp. gr. is white, and is unchanged by heating it to 250°; the less stable β-salt with the lower sp. gr. is brownish, loses weight at 40°, and on losing weight acquires a higher sp. gr. The conditions of preparation of the less stable salt are not clear. F. W. Clarke made it by the action of hydriodic acid on cadmium and on cadmium carbonate; but F. W. Short believed that the so-called β-form is an impure variety of the α-form in that the α-form with air bubbles gives the β-variety, and J. F. Snell said that the low sp. gr. form behaves like a mixture of cadmium iodide, hydrogen iodide, and water. E. Cohen and A. L. T. Mösveld confirm the existence of α- and β-CdI_2, and say that whether prepared by crystallization from soln. or by the condensation of its vapour, ordinary cadmium iodide is a mixture of these two forms, and therefore the properties usually ascribed to cadmium iodide are really the properties of a mixture.

E. Cohen and co-workers represent the **specific volume,** v, of soln. containing c grms. of CdI_2 per gram of soln. by $v=1{\cdot}00435-0{\cdot}820924c+0{\cdot}016857c^2$. W. Biltz gave 64·88 for the mol. vol. of cadmium iodide. According to S. Motylowsky, the drop weights W of molten zinc and cadmium iodides at their m.p. are respectively 46 and 58, when the **surface tension** σ is $\sigma=0{\cdot}076W$. C. A. Valson gives 50·6, 58·0,

55·8, . . . and 50·5, as the relative capillary heights h in a $\frac{1}{2}$ mm. tube of soln. of cadmium iodide containing respectively 0, 5, 10, . . . and 25 grms. of CdI_2 per 100 c.c. of water at 15° ; similarly, he obtained h=58·0, 55·8, . . . and 50·5 for soln. with 5, 10, . . . and 25 grms. of cadmium iodide in 100 grms. of water. A soln. with a grm. eq. of cadmium iodide has h=52·3, and the sp. gr. of the soln. is 1·142, at 15°, hence, Dh, the surface tension, is 60·7, a greater value than for water alone.

The **melting point** of zinc iodide is 446° ± 1°, according to T. Carnelley ;[4] 446°, according to W. Hampe ; and 450°, according to L. Graetz. For cadmium iodide, O. Ruff and W. Plato give 350° ; H. Brand, 385° ; G. Hermann, 392·4° ; and W. Hampe, and L. Graetz, 404°. According to R. Nacken, the f.p. in the cooling curve appears at 385°, and he could detect no signs of allotropic modifications in the heating or cooling curves. O. Ruff and W. Plato obtained a rounded curve with mixtures of cadmium fluoride and iodide with cadmium iodide, Fig. 43. The

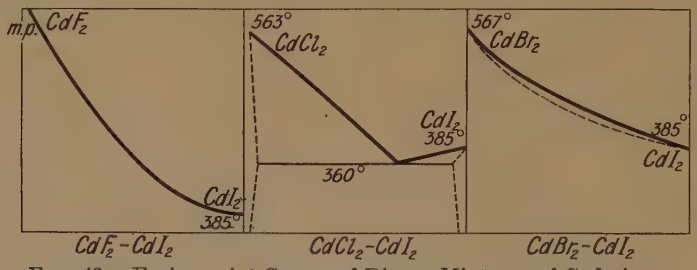

Fig. 43.—Fusion point Curves of Binary Mixtures of Cadmium Iodide with Cadmium Fluoride, Chloride, and Bromide.

latter has a minimum at about 348° and 90 molar per cent. of the iodide. R. Nacken also found the f.p. of cadmium bromide (567°) with increasing proportions of cadmium iodide falls steadily to the value for cadmium iodide, Fig. 42 ; mixtures with cadmium chloride give the typical V-eutectic at 360° with 70 molar per cent. of cadmium iodide, Fig. 42.

According to the vap. density determinations of A. Scott,[5] cadmium iodide is partially dissociated. According to E. Beckmann, the **molecular weight** of zinc iodide in boiling quinoline is 320—the calculated value for ZnI_2 is 319·1 ; and for cadmium iodide, 363—the calculated value for CdI_2 is 364·72. Hence the mol. wts. are here nearly normal. For cadmium iodide in boiling water, S. M. Johnston, E. Beckmann, and W. Landsberger find a mol. wt. 333 to 366 ; E. Beckmann found in alcohol 313 to 361 ; H. C. Jones found in acetone 448·6 to 510·7 ; S. Schröder and H. Steiner found in methyl acetate 176·8 to 183·3 ; and A. Werner found in piperidine, 365·21 ; in pyridine, 348·34 ; in methyl sulphide, 356 ; and in ethyl sulphide, 369. G. Tammann found the lowering of the vap. press. of aq. soln. corresponded with an abnormal mol. wt.

According to H. Fizeau,[6] the coeff. of **linear expansion** of crystals of cadmium iodide is 0·000029161 at 40° ; and the coeff. of expansion of the molten salt is positive and relatively large. P. Kremers has measured the **volume expansion** of soln. of zinc iodide at different temp.—vol. at 19·5° unity. With 18·8 mols of ZnI_2 in 100 parts of water, the volume at 0° is 0·99403 ; at 40°, 1·00877 ; at 60°, 1·01960 ; at 80°, 1·03249 ; and at 100°, 1·04751 ; similarly with soln. with 198·4 mols of ZnI_2, 0·98736 at 0° ; 1·01392 at 40° ; 1·02815 at 40° ; 1·02815 at 50° ; 1·04269 at 80° ; and 1·05756 at 100°. For cadmium iodide with 22·6 mols. per 100 grms. of water, 1·00863 at 40° ; 1·01935 at 60° ; 1·03218 at 80° ; 1·04667 at 100° ; and with 46·4 mols of CdI_2, 1·01027 at 40° ; 1·02198 at 60° ; 1·03523 at 80° ; and 1·04995 at 100°. In both cases the coeff. of expansion increases with increasing conc.

C. Helmreich gives the **specific heat** of cadmium iodide as 0·05264 between 0°

and 30° ; 0·05274 between 0° and 50° ; and 0·05277 between 0° and 70°. W. Timofejeff said that the sp. ht. of conc. aq. soln. of cadmium iodide is but one-third the value for alcoholic soln. ; for dil. soln., the sp. ht. is nearly the same as the solid ; C. Helmreich found for 15·16, 29·99, and 45·70 per cent. soln. the respective sp. ht. 0·87235, 0·72725, and 0·57953 between 0° and 30° ; and 0·83952, 0·70932, and 0·56936 between 0° and 70°.

J. Thomsen's [7] value for the **heat of formation** of zinc iodide from its elements (Zn, I_2)=49·23 Cals., and for cadmium iodide (Cd, I_2), 48·83 Cals. T. J. Webb obtained 49·9 Cals. for the heat of formation of zinc iodide ; and H. S. Taylor and G. S. J. Perrott gave 48·5 Cals. for the heat of formation of cadmium iodide from its elements. According to R. de Forcrand, the heat of formation of zinc iodide in aq. soln. is 61·23 Cals. J. Thomsen also gives for the **heat of solution** of a mol of zinc iodide in 400 mols of water at 18°, 11·31 Cals., and likewise for cadmium iodide, —0·96 Cal.

The **solubility** of zinc iodide in water has been determined by E. Lubarsky,[8] F. Mylius and R. Dietz, and A. Étard :

	−5°	0°	18°	40°	60°	80°	100°
Per cent. ZnI_2	80·77	81·11	81·20	81·66	82·37	83·05	83·62
Solid phase	$ZnI_2.2H_2O$			ZnI_2			

Below —7°, tetrahydrated zinc iodide, $ZnI_2.4H_2O$, is the stable form in aq. soln., and the transition point is —7° when dihydrated zinc iodide, $ZnI_2.2H_2O$, appears, and it is transformed into the anhydrous salt at 0°. The solubility curve of $ZnI_2.2H_2O$ has been extended by R. Dietz into the metastable region 10°, 82·06 ; 22°, 83·12 ; and 27°, 89·52 per cent. A. Étard gives the solubility at 140° as 83·6 per cent. J. B. Berthemot prepared **dihydrated zinc iodide,** $ZnI_2.2H_2O$, in 1828 ; and R. Dietz found that this salt separates in prismatic deliquescent crystals when a 83·5 per cent. soln. of neutral zinc iodide is cooled to —8° ; at 27° the crystals partially fuse and become anhydrous. According to E. Lubarsky, **tetrahydrated zinc iodide**, $ZnI_2.4H_2O$, crystallizes from a sat. soln. when a crystal of $ZnCl_2.3H_2O$ is added ; it melts at —7° with the formation of the dihydrated salt. It is not definitely settled whether the alleged tetrahydrated salt is not a trihydrated salt.

The solubility of cadmium iodide in water has been measured by P. Kremers,[9] A. Stromeyer, J. M. Eder, A. Étard, and R. Dietz :

	−7·5°	0°	18°	40°	50°	75°	100°
Per cent. CdI_2	43·5	44·4	46·0	48·4	49·35	52·65	56·08

Ice is the solid phase below the eutectic temp. —7·5°, and at —3·4° the solubility curve has 33·3 per cent. CdI_2, and at —2·2°, 26·5 per cent. A. Étard gives the solubilities 63·1, 70·7, and 81·5 per cent. CdI_2 respectively at 140°, 185°, and 255°. E. Cohen and co-workers represented the solubility S in grms. of cadmium iodide in 100 grms. of soln. by $S=46{\cdot}793+0{\cdot}1003(\theta-30)+0{\cdot}0003256(\theta-30)^2$; the *temperature coefficient*, $dS/dT=+0{\cdot}1003\pm0{\cdot}001$ grm. per 100 grms. of soln. per degree ; and the *pressure coefficient*, $dS/dp=0{\cdot}00390\pm0{\cdot}0002$ per cent. per atm. at 30°. No definite hydrated salts have been demonstrated.

The **specific gravities** of aq. soln. of zinc iodide by P. Kremers [10] are for soln. with w grms. per 100 grms. of water at 19·5° :

w grms. ZnI_2	21·5	46·4	85·0	126·3	177·9	232·0
Sp. gr.	1·1715	1·3486	1·5780	1·7815	1·9906	2·1853

P. Kremers, C. A. Valson, O. Grotrian, F. J. Wershoven, and many others have determined the sp. gr. of soln. of cadmium iodide. From O. Grotrian's and F. J. Wershoven's values at 18° :

Per cent. CdI_2	0·0429	0·399	1·017	4·87	10·03	19·54	29·60	44·13
Sp. gr.	0·99908	1·0021	1·0073	1·0413	1·0885	1·1890	1·3171	1·5573

A. J. Rabinowitsch measured the sp. gr. and **viscosity** of soln. of zinc and cadmium iodides.

The **lowering of the vapour pressures** of aq. soln. of cadmium iodide have been measured by J. Moser,[11] and G. Tammann; the latter found for soln. with 29·35, 59·56, and 113·22 grms. of CdI_2 in 100 grms. of water the respective lowerings 12·4, 26·4, and 55·9 mm. J. Moser found a minimum in the relative lowering of the vap. press. E. Beckmann, F. Jüttner, W. Landsberger have investigated the **raising of the boiling points** of aq. soln. of cadmium iodide. The value of J. H. van't Hoff's boiling constant varies from 1·00 to 1·05 as the conc. of the soln. rises from 0·119 to 0·651 mol of cadmium iodide per litre. F. Rüdorff, S. Arrhenius, H. C. Jones, V. J. Chambers and C. W. Frazer, and J. W. McBain have investigated the **lowering of the freezing points** of aq. soln. of cadmium iodide. The value of J. H. van't Hoff's freezing constant i falls from 2·40 to 1·24 when the conc. rises from 0·00105 to 0·1001 mol of cadmium iodide per litre.

A. des Cloizeaux[12] found the crystals of cadmium iodide have a strongly negative double refraction. J. A. Wilkinson says the fluorescence of cadmium iodide is white, the phosphorescence is feeble, and the thermoluminescence strong. P. Kremers found the **refractive indices** of soln. of zinc iodide of sp. gr. 1·4033, 1·5563, and 2·0286 at 19·5° to be respectively 1·4049, 1·4308, and 1·5090 at 15°. Similarly, for soln. of cadmium iodide of sp. gr. 1·2934 and 1·5983 at 19·5°, the refractive indices are 1·3792 and 1·4293 at 16°. C. Bender, H. Jahn, R. de Muynck, F. H. Getman and F. B. Wilson, and M. le Blanc and P. Rohland have also measured the refractive indices of soln. of cadmium iodide. According to H. Jahn, at 20°, soln. of sp. gr. 1·1541 and 1·5181 have respectively μ_α=1·3556 and 1·4142; μ_D=1·3580 and 1·4176; and μ_β=1·3634 and 1·4163. P. Barbier and L. Roux have measured the **dispersion** of soln. of cadmium iodide; and H. Jahn found the specific **electromagnetic rotation** of the plane of polarization with soln. of sp. gr. 1·1541 to 1·5181 (20°) to be nearly 2·0133, and J. Forchheimer also found the mol. magnetic rotation to be independent of the conc. or degree of ionization of the soln. C. Sheard and C. S. Morris measured the **emission spectrum** of zinc iodide and found bands between 5610 and 5535; 5195 and 5116; and between 4829 and 4780. They found some emission spectral bands with cadmium iodide, but rapid vaporization prevented accurate measurements. E. J. Evans studied the **absorption spectrum** of cadmium iodide vapour.

F. Braun[13] says that solid anhydrous zinc iodide does not conduct electricity electrolytically; M. Faraday and W. Hampe have shown that the molten iodide is a good conductor; W. Hampe makes a similar remark about cadmium iodide. L. Graetz found the **electrical conductivity,** $K\times10^8$, in Siemens' units (mercury unity) is:

	520°	500°	480°	460°	450°	440°	420°	410°
$K\times10^8$ . .	1660	1500	1325	1140	1050	630	300	30

and likewise for cadmium iodide:

	440°	420°	410°	404°	400°	380°	320°	270°
$K\times10^8$. .	3470	2780	2600	2490	2440	2175	750	2·5

There is a break in the resulting curve in passing from the solid to the liquid state. According to G. C. Schmidt and W. Hechler, the vap. of zinc iodide is an electrical conductor, and A. E. Garrett and R. S. Willows have shown that when the iodide is heated, it ionizes the surrounding gas.

G. Jäger gives for the eq. conductivity of soln. with 0·025, 0·0125, 0·00625, and 0·003125 gram-eq. of zinc iodide per litre at 22°, 103·08, 105·12, 110·56, and 115·52, respectively; and S. M. Johnston, for the eq. conductivity of soln. with 0·312, 1, 10, 1000 mols of cadmium iodide per litre, 269, 406, 984, and 3317 respectively. H. C. Jones and co-workers found the mol. conductivity, μ, and the percentage degree of ionization, α, of soln. with a mol of cadmium iodide in v litres, to be

v	4	8	32	128	512	2024
$\mu_0°$	20·45	24·31	39·45	62·73	87·06	109·01
$\mu_{65}°$	74·96	94·61	161·3	254·8	345·5	414·5
$\alpha_0°$	17·2	20·5	33·2	52·8	73·3	91·7
$\alpha_{65}°$	18·5	22·8	38·9	61·4	83·3	100·0

A. J. Rabinowitsch measured the anomalous ionization—*i.e.* the decrease in the eq. conductivity with dilution—of soln. of zinc and cadmium iodides. According to J. W. McBain, cadmium iodide is almost completely converted into a complex salt in conc. soln., and consequently, the calculations of α are uncertain because of the formation of complexes. H. C. Jones' observations show that under similar conditions, cadmium iodide ionizes less rapidly than the bromide, and the latter, in turn, less readily than the chloride. The **transport [numbers** for the anions with zinc iodide in 0·976N-, 0·488N-, and 0·248N-soln. are respectively 0·602, 0·586, and 0·579 ; and H. Jahn found that for soln. with a mol of zinc iodide in 4·02 and 300·4 litres, the transport number falls from 1·003 to 0·558. From the data for the conductivities, lowering of the f.p., and the transport numbers, J. W. McBain calculates that in a $\frac{1}{10}N$-soln. of cadmium iodide, about 80 per cent. of non-ionized iodide is present, and about half the anions are CdI_3' and half CdI_4''. Data for the transport numbers of cadmium iodide have also been given by W. Hittorf, G. Heym, R. Lenz, W. Bein, V. Gordon, G. Carrara, H. Jahn, etc. ; and for zinc iodide by W. Hittorf, and G. Kümmell.

A. P. Laurie [14] has investigated the **electrical potential** of the combinations Zn | $ZnI_{2soln.}$, I_2 | Pt at 20° and with 0·309 to 0·0006 grm. of iodine per c.c. of soln. of 0·33 grm. of ZnI_2 per gram of water the potential changes only from 1·287 to 1·221 volts ; and with 0 to 3·87 grms. of zinc iodide per gram of a solution with 0·14 grm. of iodine per c.c. from 1·594 to 1·075 volts. In the combination Zn | $ZnI_{2soln.}$, CuI | Cu, with 0 to 3·9 grms. of ZnI_2 per gram of water, the potential falls from 0·894 to 0·415 volt. Similarly, for the combination Cd | $CdI_{2soln.}$, I_2 | Pt, the potential falls from 1·087 to 1·039 volts, when the number of grams of iodine per c.c. of a one per cent. soln. of cadmium iodide changed from 0·0032 to 0·00005. T. J. Webb found that the e.m.f. of the cell Ag | Ag ⌇, ZnI_2 (sat. soln.) | Zn (amalgam) to be 0·39872 volt at 25°, and the temp. coeff. —0·000094. A. Hagenbach found for a temp. difference of 70°, the e.m.f. of the combinations Cd | CdI_2 and CdI_2 | Cd with soln. with a mol of cadmium iodide per 10 and 100,000 litres fell from 0·0623 to 0·0522 volt. E. Cohen and co-workers represented the e.m.f., E, of cadmium in cadmium soln. containing c grms. of the salt per 100 grms. of soln. at 30°, by $E=0·46338-0·0009461c-0·00000011c^2$. S. Meyer found the **magnetic susceptibility** of powdered cadmium iodide to be $-0·25\times10^{-6}$ mass units at 18°.

Zinc and cadmium iodides are among the few metal iodides soluble in *alcohol*.[15] According to J. M. Eder, at 15°, one part of cadmium iodide is dissolved by 0·98 part of alcohol of sp. gr. 0·794, or the solubility is 50·5 per cent. According to W. Timofejeff, at 20°, 100 grms. of a sat. methyl alcohol soln. contain 59·0 grms. of CdI_2 ; of ethyl alcohol, 42·6 grms. ; and of propyl alcohol, 28·9 grms. CdI_2. The sp. gr. of soln. of cadmium iodide in alcohol have been determined by G. Carrara and M. G. Levi, H. Jahn, C. Cattaneo, and by M. le Blanc and P. Rohland. At 18°, soln. with 0·4290, 0·0108, and 0·0021 mol of cadmium iodide per litre have sp. gr. 0·863, 0·796, and 0·796 respectively. The **molecular volume** of cadmium iodide in alcohol soln. has also been investigated by G. Carrara and M. G. Levi. R. Lenz has investigated the **velocity of diffusion** of cadmium iodide in alcoholic soln. ; and W. Herz and M. Lewy, the *partition* of cadmium iodide between water and amyl alcohol, and the results show either that the salt is polymerized in the alcoholic soln. or complex ions are formed. W. Timofejeff, and C. Helmreich have measured the **specific heats** of alcoholic soln. of cadmium iodide. S. Arrhenius has measured the **lowering of the freezing point** of alcoholic soln., and E. Beckmann, W. Landsberger, H. C. Jones the **raising of the boiling point.** The **indices of refraction** of soln. of cadmium iodide in alcohol have been measured by M. le Blanc

and P. Rohland, and likewise by H. Jahn, who has also measured the sp. **electromagnetic rotation** of the plane of polarized light. The **electrical conductivities** and temp. coeff. of soln. of cadmium iodide in various alcohols have been measured by N. Zelinsky and S. Krapiwin, H. C. Jones and C. F. Lindsay, W. Hampe, W. Hittorf, C. Cattaneo, R. Lenz, C. Nordmann, etc. According to H. C. Jones and C. G. Carroll, for soln. of a mol of cadmium iodide in v litres of 25 and 100 per cent. methyl and ethyl alcohol at 0°, the mol. conductivities are :

v	16	32	64	128	256
25 per cent. CH_3OH	33·83	42·10	55·02	70·22	87·31
100 per cent. CH_3OH	13·39	14·51	14·83	16·82	20·01
25 per cent. C_2H_5OH	26·97	34·90	44·21	54·54	69·71
100 per cent. C_2H_5OH	2·29	2·30	2·32	2·39	2·66

The **transport numbers** of the ions in alcoholic soln. have been measured by W. Hittorf ; and A. Campetti, and H. C. Jones find that alcoholic soln. are positive towards aq. soln. The marked tendency of cadmium iodide to polymerize or form complex ions, and its marked solubility in many non-aq. solvents, have attracted many investigators to a study of the behaviour of this salt in non-aq. solvents.

W. Hampe found cadmium iodide is soluble in anhydrous *ether*, and J. M. Eder says that the solubility in absolute ether is 21·7 per cent., and, according to C. E. Linebarger, ethyl ether at 0°, 15°, and 20·3° dissolves respectively 0·03, 0·04, and 0·05 per cent. of cadmium iodide. C. Cattaneo says the sp. conductivity of a soln. of 0·095 grm. of cadmium iodide in 100 grms. of ether referred to mercury at 0° is $0{\cdot}556 \times 10^{-12}$. W. Eidmann says zinc iodide is soluble in *acetone*, and, according to A. Naumann, the sp. gr. of a sat. soln., containing 20 per cent. of cadmium iodide, is 0·994 (18°). P. Dutoit and E. Aston have measured the conductivity and H. C. Jones the b.p. of acetone soln. of *cadmium iodide*. J. Schröder and H. Steiner give the solubility of cadmium iodide in *methyl acetate* as 0·70 to 1·50 per cent., and 2·10 per cent. at the b.p. Cadmium iodide is slightly soluble in *ethylamine*, according to F. L. Shinn, and insoluble in *allyl mustard oil*. C. E. Linebarger gives the solubility of cadmium iodide in *benzene* at 16° and 35° as 0·01 and 0·02 per cent. respectively. G. Coffetti has studied the conductivity of soln. of cadmium iodide in *nitromethane* ; P. Dutoit and E. Aston, in *propionitrile*, *methyl ethyl ketone*, and *methyl propyl ketone* ; P. Dutoit and L. Friderich, in *acetophenone* and *acetonitrile* soln. ; L. Kahlenberg, in acetonitrile soln. ; L. Kahlenberg and E. O. Ruhoff, *amylamine* soln. ; A. Werner and P. Ferchland measured the b.p. of soln. of cadmium iodide in *methyl and ethyl sulphides*, *piperidine*, and *pyridine* ; P. Walden and M. Centnerszwer found that cadmium iodide dissolves in liquid *sulphur dioxide* more readily in the presence of alkali iodides than in their absence ; M. Centnerszwer noted that the same salt is insoluble in liquid *cyanogen* ; P. Walden found that cadmium iodide is almost insoluble in *arsenic tribromide*, and soluble in *sulphur chloride*, S_2Cl_2, and in *sulphuryl chloride*, SO_2Cl_2. E. Beckmann found zinc and cadmium iodides to be soluble in *quinoline*. J. W. Klever said that 100 parts of *glycerol* at room temp. dissolve 40 parts of zinc iodide. W. Hampe said that zinc iodide is insoluble in *carbon disulphide*.

Zinc and cadmium iodides are very deliquescent salts. According to C. F. Rammelsberg,[16] conc. aq. soln. of zinc iodide give a gelatinous precipitate of zinc hydroxide on dilution. Aq. soln. are hydrolytically dissociated. A number of basic zinc iodides, or zinc oxyiodides, has been reported. W. Müller said that an oxyiodide is precipitated on cooling the clear hot filtered liquid resulting from the prolonged digestion of zinc with iodine and water ; T. Rettie has also reported zinc oxyiodides of uncertain composition to be formed by adding potash-lye in the presence of iodine to a soln. of zinc acetate. E. Tassilly heated a soln. of 20 grms. of zinc iodide, 20 grms. of water, and 0·2 grm. of zinc oxide in a sealed tube for 12 hrs. at 150°, and obtained hexagonal crystals of **zinc enneaoxydiiodide**, $9ZnO.ZnI_2.24H_2O$, which are stable in cold water, and lose no water at 120°, but are decomposed at 180°. Fine needle-like crystals of **zinc pentoxydiiodide**, $5ZnO.ZnI_2.11H_2O$, were also obtained by adding dil. ammonia to a soln. of zinc iodides ; the crystals are decomposed by water. The oxyiodides, said E. Tassilly, have a smaller heat of formation than the oxybromides, and the latter, in turn, smaller than the oxychlorides ; and for $5ZnO.ZnI_2.11H_2O$ he gave the heat of soln. as 115·5 Cals. E. Tassilly precipitated basic cadmium iodide or **cadmium**

oxydiiodide, $CdO.CdI_2.H_2O$, or Cd(OH)I, by treating a dil. soln. of cadmium iodide (1 : 10) with dil. aqua ammonia—some $CdI_2.2NH_3$ remains in soln. The crystals act on polarized light; are decomposed by water; and have a heat of soln. of 25·81 Cals. E. Tassilly also made $CdO.CdI_2.3H_2O$ by heating a conc. soln. of cadmium iodide and oxide at 200° in a sealed tube. The crystals are doubly refracting; and are not decomposed in water. G. Carrara found a small quantity of a basic iodide to be formed during the electrolysis of a soln. of cadmium iodide with a cadmium anode, and platinum cathode.

According to J. A. Buchner,[17] zinc iodide decomposes on exposure to moist air in the cold but not in dry air; J. L. Gay Lussac, and M. Berthelot have noted that when heated in air the iodine can be displaced by oxygen, and W. Hampe says that if air be not excluded when the salt is fused some zinc oxide is formed. According to D. J. P. Berridge, if zinc iodide is quite pure, it is not decomposed by light, but it is decomposed if cellulose be present; similar remarks apply to cadmium iodide. M. Berthelot found the iodides are reduced by *hydrogen* at a red heat. Unlike cadmium bromide and chloride, the iodide is oxidized by *nitrogen peroxide* at ordinary temp.: $CdI_2+NO_2=CdO+NO+I_2+66{\cdot}4$ Cals. C. F. Rammelsberg says zinc iodide is decomposed by *sulphuric acid*, forming sulphur dioxide, iodine, and zinc sulphate. According to C. F. Schönbein, *sulphur dioxide* immediately colours zinc iodide yellow and the colour disappears on warming, or on adding potassium hydroxide or ammonia. According to A. Naumann and co-workers, soln. of cadmium iodide in acetone give a white precipitate of $CdI_2.2NH_3$ with ammonia; a white precipitate of cadmium sulphide, CdS, with hydrogen sulphide—with very conc. soln., $2CdS.CdI_2$, is first precipitated; silver nitrate gives a white precipitate of silver iodide, AgI; with mercuric chloride, a mixture of cadmium chloride and mercuric iodide; with cupric chloride, a white precipitate of cadmium chloride and cupric iodide, some free iodine being simultaneously formed. An ethyl acetate soln. of cadmium iodide gives with mercuric chloride a white precipitate of cadmium chloride. H. N. Morse and H. C. Jones heated cadmium iodide with an excess of cadmium in vacuo, or in an atm. of nitrogen and obtained a product, $Cd_{12}I_{23}$, which is probably not *cadmium subiodide* but a solid soln. of cadmium in cadmium iodide. According to S. Baup, an aq. soln. of zinc iodide takes up as much iodine as it already contains, and the soln. becomes brown. The soln. is supposed to contain **zinc polyiodide,** ZnI_4, which, according to E. Rimini and F. Olivari, is soluble in fenchone. C. K. Tinkler found that the addition of the iodide of sodium, potassium, barium, magnesium, zinc, aluminium, hydrogen, ammonium, or tetramethylammonium to 0·001*N*-soln. of iodine in water changed the colour from reddish-brown to yellow, and the soln. gave identical absorption spectra. Hence it was inferred that all these soln. probably contain the same ion, *viz.*, I_3. R. G. van Name and W. G. Brown also studied the formation of zinc and cadmium polyiodides and polybromides. If **cadmium polyiodide** be CdI_4 the ionization is: $CdI_4 \rightleftharpoons CdI^{\cdot}+I_3'$. C. K. Tinkler says the polyiodide is probably CdI_3. H. M. Dawson found that cadmium iodide does not dissolve with iodine in nitrobenzene soln. C. W. Blomstrand obtained indications of the formation of an *ammonium zinc periodide*, in violet plates by the action of zinc iodide and a soln. of iodine in ammonium iodide. By passing hydrogen iodide through a mixture of solid cadmium iodide and its sat. soln. at 0°, a dark brown fuming liquid is obtained from which D. Dobroserdoff separated colourless needle-like crystals of **cadmium hydroiodide,** $CdI_2.HI.3H_2O$, on cooling to −4·7°. The crystals are stable in the mother liquid, or in an atm. of hydrogen iodide, but not in air. M. Berthelot also obtained crystals of cadmium hydroiodide by cooling to −25° a sat. soln. of cadmium iodide in hydriodic acid. E. Cornec and G. Urbain found that the f.p. of mixed soln. of cadmium iodide and hydriodic acid corresponded with the formation of $CdI_2.2HI.nH_2O$. The compound **zinc iodochloride,** $ZnCl_2.2ICl_3.H_2O$, has been indicated in connection with zinc chloride. H. Franzen and O. von Mayer[18] prepared **zinc hydrazine iodide,** $ZnI_2.2N_2H_4$, and **cadmium hydrazine iodide,** $CdI_2.2N_2H_4$.

According to G. Gore,[19] and E. C. Franklin and C. A. Kraus, zinc iodide is moderately soluble in liquid ammonia; while, according to G. Gore, cadmium iodide is insoluble, and, according to E. C. Franklin and C. A. Kraus, it is slightly soluble. Note the decreasing solubility of the zinc halides in liquid ammonia in passing from the iodide to the bromide which is slightly soluble, and the chloride and fluoride which are insoluble. C. F. Rammelsberg and E. Tassilly found that zinc iodide absorbs dry ammonia with the development of heat; and the mass swells up, forming a voluminous white powder, probably **zinc hexammino-iodide,** $ZnI_2.6NH_3$, which is decomposed by water with the separation of zinc hydroxide. Cadmium iodide under similar conditions, said C. F. Rammelsberg, forms **cadmium hexammino-iodide,** $CdI_2.6NH_3$. Zinc and cadmium hexammino-iodides were studied by F. Ephraim. He gave 65° for the decomposition temp. of the zinc salt. The spontaneous evaporation of a soln. of zinc iodide in aq. ammonia gives white bipyramidal rhombic crystals of **zinc tetrammino-iodide,** $ZnI_2.4NH_3$, with axial ratios, according to C. F. Rammelsberg, $a : b : c = 0{\cdot}7922 : 1 : 0{\cdot}5754$. F. Ephraim found the zinc salt decomposed at 199°. E. Tassilly gives the heat of soln. as 22·35 Cals., but the crystals are decomposed like the hexammino-salt by water. J. MacCrae and H. M. Dawson obtained indications of the possible formation of *cadmium tetramminoiodide*. E. Tassilly reported an ammino-iodide, $3ZnI_2.5NH_3.H_2O$, as a result of the action of zinc oxide on a soln. of ammonium iodide; this product may not be a chemical individual. F. Ephraim prepared **zinc diammino-iodide,** $Zn(NH_3)_2I_2$. E. Tassilly made octahedral crystals of **cadmium diammino-iodide,** $CdI_2.2NH_3$, by cooling a hot soln. of cadmium iodide in aqua ammonia, and as a by-product in the preparation of cadmium oxyiodide (*q.v.*). H. Grossmann also made the same compound by the action of conc. aqua ammonia or ammonia gas on cadmium iodide, and by the prolonged boiling of cadmium hydroxide with ammonium iodide. A. Naumann and W. Müller made it by the action of ammonia on an acetone soln. of cadmium iodide. A. Agrestini proposed to utilize the ready formation of these crystals as a reagent for the micro-detection of cadmium. The compound is decomposed by water; E. Tassilly gives the heat of soln. as 11·9 Cals.; and the heat of formation, 29·6 Cals. It melts when heated giving off ammonia and forming cadmium iodide. F. Ephraim and P. Mosimann made some poly-iodides—*e.g.* **zinc tetrammino-hexaiodide,** $[Zn(NH_3)_4]I_2.2I_2$; and **cadmium tetrammino-hexaiodide,** $[Cd(NH_3)_4]I_2.2I_2$. They also made some complexes with picric acid, and with *p*-dichlorobenzenesulphonic acid.

According to M. Adams,[20] when hydroxylamine is added to a conc. alcoholic soln. of cadmium iodide, the precipitate which is first formed redissolves, and when the soln. is allowed to stand, it deposits large, colourless, acicular crystals of **cadmium trihydroxylamine iodide,** $CdI_2(NH_2OH)_3$. This compound is stable; soluble in both alcohol and water; and insoluble in ether. A comparison with the other double halides emphasizes the tendency of cadmium iodide to unite with three mols of hydroxylamine.

C. F. Rammelsberg prepared deliquescent crystals of **ammonium zinc tetraiodide,** $2NH_4I.ZnI_2$, by the evaporation of a mixed soln. of the component salts over sulphuric acid. H. Croft and E. Rimbach made deliquescent crystals of **ammonium cadmium tetraiodide,** $2NH_4I.CdI_2.2H_2O$, by evaporating a soln. of the component salts in theoretical proportions. J. M. Eder says that at 15° one part of the salt dissolves in 0·58 part of water; 0·7 part in alcohol of sp. gr. 0·794; 8·9 parts in ether of sp. gr. 0·729 and in 1·8 parts of ethereal alcohol. E. Tassilly, and H. Grossmann made $CdI_2.NH_4I$ by boiling cadmium hydroxide in a soln. of ammonium iodide, some $CdI_2.2NH_3$ being formed at the same time. E. Tassilly said that the salt has $\frac{1}{2}H_2O$, H. Grossmann, H_2O, and E. Rimbach, that the salt is anhydrous, and is stable in water. J. M. Eder says that at 15° one part of the salt dissolves in 0·9 part of water; in 0·88 part of alcohol of sp. gr. 0·794; and in 2·4 parts of ether of sp. gr. 0·729. According to S. Lussana and G. Bozzola, the soln. of $NH_4I.CdI_2$ has a maximum density at 3·54°.

H. Brand found the f.p. curve of mixtures of cadmium and sodium iodides has no signs of the formation of a compound, or of solid soln. There is a simple V-eutectic at 287° with 47 per cent. NaI. E. Cornec and G. Urbain measured the f.p., and F. Bourion and E. Rouyer the b.p., of soln. of mixtures of the alkali and cadmium iodides and obtained results in harmony with the composition of the known double salts. C. F. Rammelsberg prepared deliquescent crystals **sodium zinc tri-iodide,** $NaI.ZnI_2.3H_2O$, by the evaporation over sulphuric acid of a soln. of the component salts in theoretical proportions; the corresponding **potassium zinc tri-iodide,** $KI.CdI_2$, was made in a similar way. H. Croft made **sodium cadmium tetraiodide,** $2NaI.CdI_2.6H_2O$, in a similar manner. J. M. Eder says that at 15°, one part of the salt dissolves in 0·63 part of water; in 0·86 part of alcohol of sp. gr. 0·794; and in 10·1 parts of ether of sp. gr. 0·729. H. Croft, and E. Rimbach made the corresponding **potassium cadmium triiodide,** $2KI.CdI_2$, in a similar way. H. Brand found that the f.p. curve of mixtures of potassium and cadmium iodides, Fig. 44, has a eutectic at 185° and 47·5 molars per cent. of KI. The ascending branch of the curve has two breaks corresponding with the formation of **potassium cadmium tetraiodide,** $CdI_2.2KI$, at 269° from crystals and liquid; and a transformation of the α-cubic crystals at 215° into the β-double refracting modification stable at low temp. E. Chauvenet, and G. Urbain's analysis of the thermal effect on mixing soln. agreed with the formation of potassium cadmium tetraiodide, $2KI.CdI_2$; likewise also R. G. van Name and W. G. Brown's study of the equilibrium conditions of soln. of the component salts. F. W. Clarke's value for the sp. gr. of the salt at 21° is 3·359. One part of the clear deliquescent crystals, says J. M. Eder, dissolves at 15° in 0·73 part of water; in 1·4 parts of alcohol of sp. gr. 0·794; and in 34·5 parts of ether, of sp. gr. 0·729. The sp. gr. of soln. of the salt have been measured by O. Grotrian; the lowering of the f.p. of soln. of the salt, by H. C. Jones and F. H. Getman, and by H. C. Jones and B. P. Caldwell; the electrical conductivity by O. Grotrian, F. J. Wershoven, C. Immerwahr, and J. W. McBain; and the transport number by W. Hittorf. J. H. Walton says that like other soluble iodides K_2CdI_4 decomposes hydrogen peroxide with the evolution of oxygen.

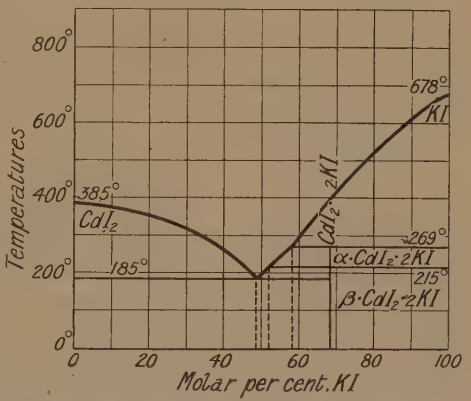

FIG. 44.—Equilibrium Curves of Binary Mixtures of Cadmium and Potassium Iodides.

In passing along the series of bivalent metals from magnesium to zinc, cadmium, and mercury, the variety of double salts increases with the at. wt. of the metal; for example, mercury gives six types of double salt with cæsium, and there are three with cadmium, two with zinc, and one with magnesium. The three **cæsium cadmium tetra- and penta-iodides** with $CsI : CdI_2 = 3 : 1$, $2 : 1$, and $1 : 1$ were prepared by H. L. Wells and P. T. Walden like the corresponding bromides. Cæsium cadmium iodide, $CsCdI_3.H_2O$, or $CsI.CdI_2.H_2O$, is obtained in thin plates from a soln. with the component salts in the mol. proportions 1 : 1. The two **cæsium zinc tetra- and penta-iodides,** 3 : 1 and 2 : 1, were made by H. L. Wells and G. F. Campbell like the corresponding chlorides and bromides. The existence of the zinc salts 1 : 1 was suspected in the syrupy liquid obtained by crystallizing the 2 : 1 salt. In view of the fact that cæsium usually forms more stable and less soluble double halides than the other alkali metals, it is remarkable that there should be a difficulty in preparing the 1 : 1 type of cæsium zinc halides when the

ammonium, sodium, and potassium zinc iodides, as well as the 1 : 1 cæsium magnesium chloride and bromide, can be readily obtained.

According to G. Hermann, cuprous and cadmium iodides form a single series of solid soln. with a minimum in the m.p. curve at 350° and 90 per cent. of cadmium iodide. C. R. Rammelsberg made **barium zinc tetraiodide,** $BaI_2.ZnI_2.H_2O$, in a similar manner to the process employed for the potassium salt; and H. Croft made **barium cadmium tetraiodide,** $BaI_2.CdI_2.5H_2O$; and H. C. Jones and B. P. Caldwell made **strontium cadmium tetraiodide,** $SrI_2.CdI_2.8H_2O$, by evaporating a soln. of equi-mol. proportions of the component salts, and they measured the mol. conductivities of the soln.

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§ 15. Zinc and Cadmium Sulphides

According to E. Schütz,[1] zinc has a greater affinity than lead for sulphur, but a smaller affinity than manganese, copper, nickel, iron, or tin; J. Fournet found the affinity of zinc for sulphur to be greater than that of lead, silver, antimony, or arsenic, and smaller than that of copper, iron, or tin; and E. Schürmann said the affinity of zinc for sulphur is greater than that of nickel, cobalt, iron, arsenic, thorium, or manganese; and he gives the order cadmium, antimony, tin, and lead. E. F. Anthon gives the order silver, copper, lead, cadmium, iron, nickel, cobalt, and manganese. A. L. Orlowsky also studied the affinity of the elements for sulphur. B. G. Bredberg assumed that some zinc ores contain *zinc subsulphide*, Zn_2S, but K. Friedrich added that this is not probable. There are no signs of the formation of zinc subsulphide when sulphur and zinc sulphide are melted together.

Zinc sulphide occurs in nature crystallized in two different forms—the one, the common zinc blende, or sphalerite crystallizes in the cubic system; and the other, the comparatively rare wurtzite, belongs to the hexagonal system. The purer forms of both are straw-coloured, although E. S. and J. D. Dana [2] state that specimens of blende from Franklin (New Jersey), and from Nordmark (Sweden) are white, and they have been called *cleiophane*. Although zinc blende is perhaps the most widely distributed mineral containing zinc, it does not appear to have attracted the attention of the early mineralogist. The mineral has a superficial resemblance to galena, except in its cleavage, but it yields no metal when smelted, and therefore it was called by G. Agricola, *galena inanis*, and by J. G. Wallerius, *pseudo-galena*. The German mining term *blende* was then employed from *blenden*, to deceive; and was also called by E. F. Glocker, *sphalerite*, from σφαλερός, deceptive. The presence of zinc in blende was first demonstrated by G. Brandt in 1735, and zinc was extracted from the mineral by A. von Swab in 1738. M. Malouin prepared zinc sulphide in 1743, and for a time it was thought to be different from the natural sulphide. T. Bergman analyzed phosphorescent blende in 1779. Analyses of zinc blende have been reported by J. A. Arfvedson, A. Löwe, C. Kersten, C. Kuhlemann, T. H. Henry,

J. L. Smith, T. Scheerer, E. Bechi, A. Breithaupt, L. Lecanu, P. Berthier, J. B. J. D. Boussingault, C. U. Shepard, A. Osann, J. Loczka, L. Sipöcz, W. Eitel, etc. Zinc blende containing gallium has been reported by L. de Boisbaudran, C. Rimatori, H. B. Cornwall, and J. B. Kirkland; mercury by P. Soltsien; tin by A. Stelzner and A. Schertel; indium by F. L. Bartlett; cadmium by C. Rimatori, A. Schmidt, A. Frenzel, and O. Herting; lead and manganese by O. Herting; cobalt by F. A. Genth; and rare earths by J. Strishoff, and S. Samailoff. F. Sandberger found lithium in the wurtzites but not in the blendes which he examined. W. N. Hartley and H. Ramage found spectroscopically iron, copper, silver, and traces of potassium and sodium in all the blendes they examined, and cadmium, gallium, indium, thallium, lead, nickel, chromium, and calcium in many other specimens.

The hexagonal variety of zinc sulphide, occurring in the silver mine, Oraro (Bolivia), was named by C. Friedel wurtzite, after A. Wurtz; the cadmiferous hexagonal blende from Pribram was named *pribramite* by J. J. N. Huot, and another variety *spiauterite*—from *spiauter*, spelter—by A. Breithaupt. Analyses of wurtzite have been made by A. Löwe, J. F. Malaguti and J. Durocher, J. Gerstendörfer, W. Stahl, H. Traube, etc. The mineral *voltzite* or *voltzine* is an oxysulphide, ZnO.4ZnS, found as a yellow incrustation at Pontgiband, France, and at Joachimsthal, Austria. It is probably a mixture of oxide and sulphide. Hexagonal cadmium sulphide, *greenockite*, was found by R. Jameson at Bishoptown (Scotland), and named after Lord Greenock. This mineral was further investigated by A. Connell, A. Breithaupt, and W. Nicol; D. Forbes called it *cadmium blende*. Analyses of greenockite have been made by A. Connell, T. Thomson, A. K. Christomanos, and E. Schüler.

Zinc sulphide has been observed as a furnace product by J. F. L. Hausmann,[3] B. von Cotta, W. Stahl, J. D. Robertson, C. C. von Leonhard, C. F. Plattner, C. W. C. Fuchs, J. H. L. Vogt, etc. J. J. Nöggerath and G. Bischof found some zinc sulphide a few inches in thickness deposited on the woodwork of an old lead mine; it is thought to have been formed by the reducing action of decaying wood upon zinc sulphate. H. A. Wheeler found blende in lignite; W. P. Jenney in coal; C. R. Keyes found blende crystals on iron nails immersed 15 yrs. in mine water; W. P. Jenny, J. D. Robertson, M. W. Iles and J. D. Hawkins also found deposits of blende in mines; and J. Delanour also observed a deposit of zinc sulphide from some spring water where it was probably formed by the reduction of zinc sulphate by organic matter.

The preparation of zinc and cadmium sulphides.—When zinc filings are heated with sulphur, the sulphur volatilizes before combination occurs, but J. Davy [4] made a little white zinc sulphide by passing sulphur vapour over red-hot zinc. The m.p. of the product is high, and it forms a protective film on the surface of the particles of metal. T. Griffiths and J. Cawley passed zinc vap. into a chamber containing sulphur vapour at a higher temp. than the b.p. of that element. An intimate mixture of zinc dust and sulphur inflames when struck by a hammer. H. Schwarz, and A. Cavazzi converted zinc filings into sulphide by heating them in a stream of carbon disulphide vapour; W. Fränkel passed nitrogen charged with the vapour of carbon disulphide over red-hot zinc, and obtained zinc sulphide and carbon. J. J. Berzelius found zinc filings withdraw the sulphur from potassium polysulphide, and the reaction is explosive if heat be applied; he also made zinc sulphide by heating mercuric sulphide with zinc—the reaction is explosive, and the mercury volatilizes. J. C. C. Dehne, and C. M. Despretz heated zinc oxide with sulphur and obtained "un product tellement identique avec la blende, que des minéralogistes exercés n'ont pu distinguer ces deux combinaisons l'une de l'autre."

J. Milbauer gradually added zinc or cadmium oxide to molten potassium thiocyanate, and obtained amorphous zinc or cadmium sulphide. E. Weinschenk obtained an amorphous powder of cadmium sulphide by heating cadmium thiocyanate with acetic acid in a sealed tube for 4–5 hrs. at 238°–250°. E. T. Allen and J. L. Crenshaw found that zinc salts do not react with sodium thiosulphate in the

cold, but at 100° the zinc is quantitatively precipitated as amorphous sulphide : $4Na_2S_2O_3+ZnSO_4=4Na_2SO_4+ZnS+4S$. Some sulphur dioxide, and hydrogen sulphide are formed by secondary reactions. J. Landauer obtained amorphous cadmium sulphide by heating cadmium oxide with anhydrous sodium thiosulphate in a sealed tube ; F. Faktor heated dried cadmium chloride with sodium thiosulphate ; and E. Donath treated a soln. of cadmium chloride or sulphate with ammonia, added an excess of acetic acid, and then treated the boiling soln. with sodium thiosulphate ; after boiling for about half an hour, the cadmium was completely precipitated as sulphide admixed with free sulphur.

K. Brückner found that zinc sulphide is formed with the evolution of sulphur dioxide when anhydrous zinc sulphate and sulphur are triturated together. L. N. Vauquelin, and A. Violi obtained the sulphide by heating the anhydrous sulphate with sulphur, J. L. Gay Lussac washed the unreduced sulphate from the mass with water, or converted it into sulphide by another ignition with sulphur. P. Berthier reduced zinc sulphate by heating it with charcoal ; if the temp. be too high, much oxide is formed. The oxide may be extracted from the sulphide by means of dil. hydrochloric acid.

E. T. Allen and J. L. Crenshaw obtained the amorphous sulphide by the action of hydrogen sulphide on zinc carbonate and hydrocarbonate ; by heating amorphous zinc sulphide with sodium hydrocarbonate, P. Farup [5] obtained coarse flecks of zinc sulphide, which could be easily filtered, by the action of hydrogen sulphide on a soln. of a zinc salt containing some hydrogen peroxide, and warming for 4 or 5 mins. to 60° or 70°. Zinc sulphide is precipitated from soln. of zinc cyanide by hydrogen sulphide ; and A. Vita precipitated zinc as sulphide from ammoniacal soln. of certain low-grade zinc ores. E. T. Allen and J. L. Crenshaw found that the precipitate obtained by adding alkali sulphides to a soln. of a zinc salt in the cold, or at a boiling temp., is always amorphous ; but if conc. soln. of alkali sulphides are employed at a higher temp., sphalerite is obtained—wurtzite is never formed. With cadmium salts under similar conditions no crystalline product was obtained, although with ammonium sulphide crystals of greenockite were formed. V. Bermont used sodium sulphide as the precipitating agent with an ammoniacal soln. of a zinc salt ; and W. Minor with an ammoniacal soln. of a cadmium salt. H. W. de Stucklé precipitated zinc sulphide from soln. of barium zincate by barium sulphide, and from soln. of alkali zincate by alkali sulphide. J. T. Norton heated soln. of zinc sulphate with sodium thiosulphate at 140° to 200°, and obtained a mixture of sulphur and zinc sulphide ; and M. le Blanc and K. Schick obtained zinc sulphide by the alternating current electrolysis of a soln. of sodium thiosulphate between zinc electrodes. R. Lorenz obtained cadmium sulphide by the electrolysis of a soln. of an alkali chloride, nitrate, or sulphate between a cupric sulphide cathode and a cadmium anode ; M. le Blanc also experimented on this subject.

H. de Sénarmont,[6] and H. Baubigny prepared sphalerite by heating a soln. of a zinc salt with hydrogen sulphide in a sealed tube ; and J. Durocher, by heating zinc chloride in a stream of hydrogen sulphide. E. T. Allen and J. L. Crenshaw obtained only the amorphous sulphide by this process, but they obtained good crystals of sphalerite by heating amorphous zinc sulphide in a soln. of sodium sulphide at 350° in a steel bomb ; the same mineral was obtained in acid soln.—*vide* wurtzite—sphalerite is alone formed in alkaline soln. ; here again E. T. Allen and J. L. Crenshaw obtained only the amorphous sulphide. A. Villiers obtained crystalline zinc sulphide by heating amorphous zinc sulphide, precipitated from a feebly alkaline soln., for one minute between 70° and 100° ; by adding ammonium chloride to amorphous zinc sulphide as precipitated from an alkaline soln. ; and by freezing an alkaline soln. in which amorphous zinc sulphide is suspended. Sphalerite crystallizes from a soln. of zinc sulphide in molten sodium chloride and potassium polysulphide, provided the temp. be below 1020° ; thus, P. Hautefeuille stated that blende is transformed into wurtzite when heated to redness, and he heated zinc or cadmium sulphide covered with a layer of alumina in a graphite crucible ; the

wurtzite or greenockite crystallized on the alumina. A. Mourlot crystallized zinc sulphide by heating it in an electric arc furnace. F. Beijerinck transformed amorphous into crystalline cadmium sulphide by heating it in a sealed glass tube. J. J. Berzelius, and H. Rose heated precipitated zinc sulphide in a stream of hydrogen sulphide. O. Rohde found amorphous zinc sulphide becomes crystalline when subjected to a press. of 8000 atm.—*vide* the action of sulphur on zinc. H. St. C. Deville and L. Troost fused together equal parts of zinc sulphate, calcium fluoride, and barium sulphide, and obtained crystals of wurtzite; with cadmium sulphide in place of zinc sulphate, crystals of greenockite were formed. They also prepared wurtzite by passing hydrogen over red-hot zinc or cadmium sulphide; the sulphide was decomposed, and redeposited in a crystalline form in the cooler parts of the tube as the hydrogen sulphide and zinc recombined; W. Biltz used an atm. of nitrogen. R. Lorenz obtained crystals of wurtzite and greenockite by acting on the vapour of zinc or cadmium with hydrogen sulphide. T. Sidot prepared wurtzite or greenockite by heating zinc or cadmium oxide in the vapour of sulphur; and he found wurtzite is formed when amorphous zinc sulphide is heated in an atm. of nitrogen, or sulphur dioxide. A. Gautier passed the vapour of carbon disulphide over heated zinc oxide; the experiments did not succeed when other zinc salts were used, or when carbonyl sulphide was employed.

E. Schüler, and R. Schneider prepared crystals of wurtzite and greenockite by fusing precipitated zinc or cadmium sulphide with potassium carbonate and sulphur. M. J. Fordos and A. Gélis, and C. Geitner heated metallic cadmium with sulphurous acid in a sealed tube at 200°, and obtained a mixture of amorphous and crystalline cadmium sulphide. E. T. Allen and J. L. Crenshaw obtained only amorphous zinc sulphide by the action of metallic zinc on sat. sulphurous acid. J. Uhl heated cadmium to redness in a stream of sulphur dioxide and obtained a mixture of cadmium sulphate and the crystalline sulphide. A. Ditte dissolved amorphous cadmium sulphide in ammonium hydrosulphide, at 60°, and obtained crystals of greenockite and free sulphur on cooling. V. Stanek heated zinc sulphide with ammonium sulphide in a tube at 150° to 200°, and obtained crystals of sphalerite, but E. T. Allen and J. L. Crenshaw succeeded in making only the amorphous sulphide; with cadmium and ammonium sulphides, in a sealed tube at 150°–200° for 3 days, greenockite crystals were formed. H. Viard prepared crystalline zinc and cadmium sulphides by passing a stream of carbon dioxide charged with the vapour of zinc or cadmium chloride over red-hot stannous sulphide. E. T. Allen and J. L. Crenshaw obtained wurtzite by subliming zinc sulphide between 1200° and 1300°, and also by the action of hydrogen sulphide derived from sodium thiosulphate, on acid soln. of zinc sulphate at 250°; similarly, also with soln. of cadmium sulphate. They obtained crystals of greenockite by heating amorphous cadmium sulphide with 30 per cent. sulphuric acid in a sealed tube for 2 days at 200°.

Zinc sulphide was found by E. Schürmann to be precipitated before nickel, cobalt, iron, arsenic, thorium, or manganese by incompletely saturating a hot $\frac{1}{10}N$-soln. of a zinc salt by hydrogen sulphide; J. C. A. Meyer observed that hydrogen sulphide precipitated iron and lead sulphides before the zinc sulphide from an acetic acid soln. of iron, lead, and zinc salts. W. Büddeus precipitated zinc sulphide alone from lye containing iron (ic), cobalt, nickel, and manganese either by the action of hydrogen sulphide, or of a sulphide and acid. J. Lefort and P. Thibault found that the presence of gum arabic in soln. of zinc salts hinders the precipitation of zinc sulphide by hydrogen sulphide.

In the analytical classification of elements, zinc is included in the group of elements which are not precipitated from acid soln. by hydrogen sulphide. If a current of this gas be passed into a sat. soln. of zinc chloride, part of the metal is precipitated as sulphide and hydrochloric acid is formed: $ZnCl_2+H_2S=ZnS+2HCl$, so that the soln. becomes acid; when the acid has attained a certain conc., the action apparently ceases. The reaction, indeed, is reversible. No precipitation occurs if over 4 c.c. of hydrochloric acid of sp. gr. 1·12 be present per 100 c.c. of soln.

According to H. Baubigny, the accumulation of hydrochloric acid can be prevented by the use of salts of certain organic acids—ammonium or sodium formate, acetate, etc. These substances react with the hydrochloric acid, producing sodium or ammonium chloride and the corresponding organic acid. The solubility of zinc sulphide in these organic acids is small enough to be neglected in certain analytical operations. According to S. Glixelli, the action of hydrogen sulphide on zinc salts does not depend on the balanced reaction : $ZnCl_2+H_2S \rightleftharpoons ZnS+2HCl$. He said the reaction is not reversible, but a kind of false equilibrium occurs in acid soln. L. Bruner, and G. Bruni and M. Padoa showed that the precipitated zinc sulphide may change into a less soluble form when it has been allowed to stand for some time. For the more soluble α-ZnS, in acid soln., S. Glixelli found $K[H]^2=[Zn]^2[H_2S]$, where $K=45\times10^{-4}$; and for the less soluble β-ZnS precipitated from alkaline soln., $K=1\times10^{-2}$. L. Bruner and J. Zawadzky considered that these numbers cannot be exactly determined because of the rapidity of the change α-ZnS$\rightarrow\beta$-ZnS. S. Glixelli found that the state of false equilibrium was favoured by the presence of silicic acid, zinc, cadmium or copper sulphide. G. Bruni and M. Padoa found that if air or hydrogen be passed through the liquid from which cadmium sulphide has been precipitated by hydrogen sulphide, the precipitate redissolves. S. Glixelli was able to obtain precipitates from rather conc. acid soln. provided sufficient time be allowed. E. T. Allen and J. L. Crenshaw have plotted the conc. of zinc in soln. as they vary with the conc. of the sulphuric acid, after precipitation with hydrogen sulphide at one atm. press. has ceased ; the results are shown in Fig. 45, where the shaded portion represents the zinc remaining in soln. This subject is rather important in analytical work, when zinc is precipitated as sulphide from faintly acid soln. It has been discussed by C. W. Eliot and F. H. Storer, E. Grundmann, F. C. Calvert, etc. H. A. Fales and G. M. Ware show that the least error occurs when the acidity of the soln. represented in terms of the conc. of the H·-ion is between 10^{-2} and 10^{-3}. This is illustrated in Fig. 46, where the ordinates represent

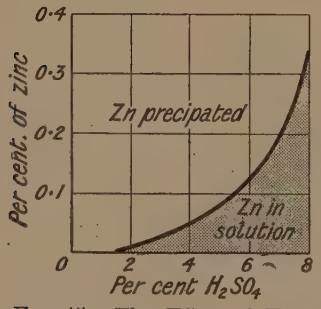

Fig. 45.—The Effect of Free Sulphuric Acid on the Precipitation of Zinc Sulphide.

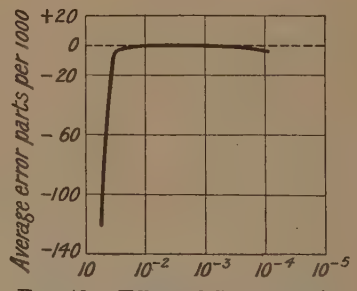

Fig. 46.—Effect of Concentration of Hydrogen Ion on the Precipitation of Zinc as Sulphide.

the average error produced when zinc sulphide is precipitated from 200 c.c. of a soln. containing a gram of ammonium zinc sulphate, $Zn(NH_4)_2(SO_4)_2.6H_2O$. If the conc. of the H·-ion exceeds 10^{-2} the completeness of the precipitation rapidly falls, and if the conc. of the H·-ion is less than 10^{-3}, the precipitate becomes slimy and difficult to filter. The favourable conc. of H·-ion is obtained conveniently by using ammonium formate, or citrate. E. T. Allen and J. L. Crenshaw also found that the zinc sulphide precipitated from neutral or acid soln. at temp. below 200°, is always amorphous ; and observations on the influence of temp. and acidity of soln. on the crystalline form of zinc sulphide are summarized in Table IV, where *W* represents wurtzite, *S* sphalerite, and *A* the amorphous form of zinc sulphide. A. L. T. Mösveld also found that in acid soln. wurtzite is precipitated, and in neutral or faintly alkaline soln., sphalerite separates.

TABLE IV.—THE EFFECT OF TEMPERATURE AND ACID CONCENTRATION ON THE CRYSTALLINE FORM OF ZINC SULPHIDE.

Temp.	Percentage amount of H_2SO_4					
	1·0	2·5	4·0	5·0	7·5	10·0
250°	*S* and *W*	*W* and *A*	—	*W* and *A*	—	—
300°	no *W*; little *A*	no *W*	70% *W* and *A*	5% *W*	90% *W*	all *W*
350°	—	70% *W*	—	30% *W*	—	80% *W*

The conditions of temp. and final acid conc. necessary for the genesis of either form of zinc sulphide are illustrated in Fig. 47. A. Kohner found that cadmium sulphide, precipitated from neutral soln., always contained some free sulphur, and R. Meldrum obtained amorphous cadmium sulphide from neutral soln. of cadmium salts, even after standing for a long time, or after boiling; and E. Donath and J. Mayrhofer obtained only amorphous cadmium sulphide with alkali sulphide as precipitating agent. E. A. Partridge studied the preparation of pure cadmium sulphide from cadmium sulphate and hydrogen sulphide.

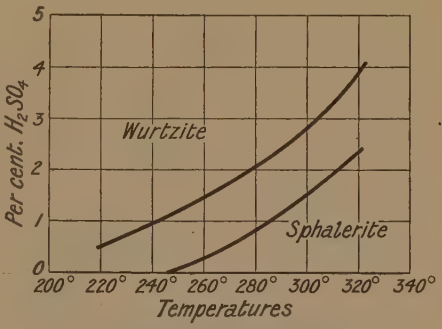

FIG. 47.—Fields of Precipitation of Sphalerite and Wurtzite.

G. Bruni and M. Padoa, and H. Baubigny found that by raising the press. of the hydrogen sulphide the equilibrium $H_2S+ZnCl_2 \rightleftharpoons 2HCl+ZnS$ was displaced in favour of the right side. Similarly with cadmium salts. Acidified soln. of cadmium sulphate which precipitate cadmium sulphide when treated with hydrogen sulphide at ordinary press., give no precipitate if the gas be under reduced pressure. M. Padoa and L. Cambi obtained the results indicated in Table V, where the number in the press. column

TABLE V.—THE EFFECT OF PRESSURE ON THE FORMATION OF ZINC AND CADMIUM SULPHIDES.

Normality of acid.	0·2 mol $ZnSO_4$ (19°).	0·1 mol $ZnSO_4$ (19°).	0·1 mol $ZnCl_2$ (13°).	0·01 mol $ZnCl_2$ (16°).
	Press. mm.	Press. mm.	Press. mm.	Press. mm.
0·2	139	150	95	170
0·4	210	320	210	380
0·6	390	490	310	620
0·8	540	610	480	—
1·0	620	760	—	—

N-HCl	0·2 mol $CdCl_2$ (14°).	0·1 mol $CdCl_2$ (14°).	0·05 mol $CdCl_2$ (14°).	0·025 mol CdCl (13°).
	mm.	mm.	mm.	mm.
0	15	15	15	15
0·5	15	15	15	30
1·0	20	20	30	60
1·5	35	60	80	130
2·0	87	140	225	340
2·5	200	310	540	—
3·0	570	—	—	—

represents the smallest press., in mm. of mercury, which is required for the production of cadmium or zinc sulphide. W. N. Stull found the reaction between hydrogen sulphide and hydrochloric or sulphuric acid soln. of zinc salts is exceedingly slow, and in no case was equilibrium attained after the soln. had been treated many hours with a rapid stream of the gas. The course of the reaction in either case is virtually the same. Agitation had no appreciable influence on the results; and a difference of temp. between 20° and 50° had very little influence. Similar results were obtained with a soln. of cadmium salts in sulphuric or hydrochloric acid; the crystallinity of the precipitate depends on the acidity of the soln., the temp., etc.

T. Sidot[7] synthesized **phosphorescent zinc sulphide**—*Sidot's blende*—by heating crystalline zinc sulphide for 4 or 5 hrs. in a porcelain tube in a stream of sulphur dioxide; C. Henry made it in large quantities by precipitating a neutral soln. of pure zinc chloride with ammonia, redissolving the precipitate in excess of ammonia, and then exactly precipitating with hydrogen sulphide. The precipitate is carefully washed and dried, and is then heated almost to a white heat in a fire-clay crucible placed inside a plumbago crucible, brasqued with charcoal. The brilliancy of the phosphorescence seems to depend on the purity of the zinc sulphide, and the product is either non-phosphorescent or feebly phosphorescent if zinc oxide or any zinc salt other than the chloride is used, or if alkali sulphides are used as the precipitant in place of hydrogen sulphide. Manganese sulphate, lead acetate, lithium carbonate, thallium carbonate, strontium chloride, basic bismuth nitrate, etc., all prevent phosphorescence. K. A. Hofmann and W. Ducca made it by C. Henry's process from commercial zinc chloride, but not from chemically pure zinc ammonium sulphate. If 5 grms. of sodium chloride and 0·2–0·5 grm. of magnesium chloride are added to 20 grms. of pure zinc ammonium sulphate dissolved in 400 c.c. of water, and the precipitate, with hydrogen sulphide, is dried without being washed, the yellow, crystalline zinc sulphide, which remains after heating, is highly phosphorescent. Contrary to C. Henry's statement, the phosphorescence must be due to the presence of traces of the sodium and magnesium salts. The addition of sodium chloride or of magnesium chloride alone does not cause the phosphorescence. The presence of traces of iron, nickel, cobalt, bismuth, chromium, or copper salts diminishes, but traces of salts of tin, selenium, manganese, or cadmium increase the effect. According to H. Grüne, pure zinc sulphide is not phosphorescent, but the addition of a trace of copper, silver, lead, bismuth, tin, uranium, or cadmium causes it to become so. Copper produces the best result, 1 part of copper in 10,000 causing a beautiful green phosphorescence. The addition of manganese, on the other hand, produces a yellowish-red phosphorescence, and the zinc sulphide in this case, when scratched or rubbed, emits light spontaneously. W. P. Jorissen and W. E. Ringer found the results obtained with zinc sulphide resembled those with the sulphides of the alkaline earths. The pure sulphide of cadmium, barium, or zinc does not phosphoresce except in the presence of traces of foreign matter such as bismuth salts. In the case of zinc sulphide, it is found that whereas magnesium chloride or sulphate has no action, bismuth, cadmium, or manganese salts and the chlorides of sodium or potassium produce a marked effect. The phosphorescence caused by the two latter substances is increased by the addition of manganese salts, is diminished by copper salts, and is entirely suppressed by platinum and silver salts.

A. Karl heated a mixture of manganese nitrate with five times its weight of zinc sulphide in an electric furnace at 1200°, the cold mass was washed in water and dried. The manganese nitrate can be replaced by stannic oxide, titanic oxide, silica, zirconia, didymium oxide, manganese silicate or stannate, etc. The product is strongly triboluminescent; with zinc sulphide alone, it is feebly so. K. Albert found that by calcining zinc sulphide with sodium chloride a phosphorescent product is formed which is not removed by washing; if heated with alkali sulphides, polysulphides, or hydrosulphides, the sensitiveness is diminished. H. W. de Stucklé

said that zinc sulphide becomes insensitive to light if the precipitated sulphide is dehydrated so that the ratio $H_2O : ZnS$ is no more than 1 : 5. J. Cawley found the precipitate obtained by the addition of alkaline earth sulphides to soluble zinc salts, when calcined, washed, and powdered, is phosphorescent. J. Schmidt, and E. Tiede and A. Schleede described the preparation of highly phosphorescent zinc sulphide.

The physical properties of zinc and cadmium sulphides.—The **colour** of zinc sulphide is white or pale yellow (if cadmiferous). Sphalerite is white when pure, but when ferruginous, it is variously coloured, yellow, brown, or black. Wurtzite is usually brown, but when prepared artificially it is colourless. Amorphous cadmium sulphide is coloured yellow, orange, or brown. According to E. T. Allen and J. L. Crenshaw,[8] fresh rapidly precipitated zinc sulphide has spherical particles 0·0002 to 0·0005 mm. diameter; while the particles of the slowly precipitated sulphide increase in size, and aggregate into clusters or crusts when allowed to stand in the soln. When the aggregates are compressed under a cover glass, they flatten and break open like a stiff jelly. The jelly-like globules contain very little water, the crusts and globules may harden and become brittle and gritty, and exhibit a refractive index for Li-light between 2·18 and 2·25, which is smaller than the refractive index of sphalerite or wurtzite. The double refraction exhibited by the amorphous sulphide is probably caused by strains induced in non-homogeneous masses during the process of hardening. When heated above 200°, the amorphous crusts and globules become wholly or partially crystalline. Amorphous cadmium sulphide has not been observed in a hard, brittle, doubly refracting form like zinc sulphide, and when it exhibits double refraction, its refractive index approaches that of greenockite.

Cadmium sulphide is used as a paint—*cadmium yellow*, *Cadmiumgelb*, *jaune de cadmium*—varying in colour from lemon-yellow to a deep orange. Admixtures of cadmium yellow and white-lead are known in commerce as *jaune brillant*. This colour is inclined to darken owing to the formation of black lead sulphide. According to O. Follenius, the different tints are due to the presence of variable amounts of impurity, but G. Buchner claimed that this hypothesis cannot be right because samples with variable amounts of impurity may have the same tint; and samples of different tint may have the same amount of impurity. G. Buchner, and N. von Klobukoff hold that the differences in colour are due to the existence of two modifications—one, **α-cadmium sulphide,** is lemon-yellow, the other, **β-cadmium sulphide,** is vermilion; the latter is assumed to be a polymeride of the former, and variations in the colour of cadmium sulphide are due to admixtures of these two forms in different proportions. The yellow variety is said to be readily polymerized into the red variety by dil. acids and alkalies; hence, on precipitating soln. of cadmium salts with hydrogen sulphide, at first the yellow sulphide forms, but, as the liberated acid comes into action, the red sulphide is precipitated, and if the soln. is acid beforehand, little or no yellow sulphide is produced. The red variety passes through the yellow stage when dissolved in acids. Sodium sulphide produces the yellow sulphide in dil. soln. of a cadmium salt, a reddish precipitate in strong soln., and a brick-red one in boiling soln. Polysulphides of potassium or ammonium precipitate the yellow cadmium sulphide mixed with varying quantities of finely divided sulphur, which can be extracted by carbon bisulphide. N. von Klobukoff found (i) the sp. gr. of the yellow varieties to vary from 3·906 to 4·147, and that of red varieties from 4·476 to 4·513; (ii) the yellow variety to be hexagonal—the red has not been determined with certainty, but shows regular and monoclinic forms; and (iii) the yellow to change to red under the influence of friction, press., heat, chemical agents, etc.

The crystals of cadmium sulphide are yellow when in tufts of hair-like needles, but larger crystals are brownish-yellow. The different colours of amorphous cadmium sulphide are due to the relative amounts of light transmitted and reflected, since the colour of a substance by reflected light depends on the character and relative amounts of light reflected directly from the external surfaces, and indirectly from internal surfaces—*i.e.* after having passed into the substance and been reflected

out. Greenockite absorbs the blue and violet and part of the green spectral rays, the remainder are freely transmitted ; a comparatively large amount of blue light is directly reflected by the plane bright faces of the crystals about 1 mm. in diameter, and a small amount of red, orange, yellow, and green is reflected after passing through the surface layer. The combined effect of all the reflected light is a lustrous dark yellow to yellowish-green or dark citron-yellow. Crystals 0·01 mm. in diameter reflect about the same amount of blue light directly, and much more of that which has penetrated the surface so that the resulting colour is a brilliant yellow. Massed crystals with a dull surface have a light yellowish-brown or citron colour. The grains of powdered crystals usually have bright but not plane surfaces and give a brilliant orange powder, for there is less direct reflection, and more indirect reflection of light from the interior which has lost more green and yellow than with a powder having plane-faced fragments. The colour of the amorphous sulphide is explained in a similar manner. The amorphous sulphide absorbs more strongly in the yellow and green and, by transmitted light, its colour is orange-yellow in films 0·01 mm. thick, and yellow in films 0·001 mm. thick. The powdered amorphous sulphide with grains 0·0001 to 0·001 mm. in diameter is bright yellow with a tinge of orange, and with grains 0·004 to 0·007 mm. in diameter, or compact aggregates of smaller globules, is bright orange. According to E. T. Allen and J. L. Crenshaw, a soln. of about 200 c.c. of water, 4 grms. of sodium sulphate, 10 grms. of sodium thiosulphate, and 2 grms. of cadmium sulphate was boiled for some hours, and hot water added from time to time. The particles of the lemon-yellow precipitate obtained after an hour's boiling were too small to measure ; but after 2½ hrs.' boiling the particles were 0·001 mm. in diameter ; as the boiling continued, the particles became darker and darker until the precipitate had acquired a dark orange colour, and the particles ranged up to 0·05 mm. in diameter. The light yellow precipitate formed by the action of ammonium sulphide on a cadmium salt retains the same colour after it has been heated so as to produce crystalline greenockite ; and the latter becomes orange coloured when ground in a mortar. Hence, the difference in colour is not due to a difference in crystalline form. The difference in the sp. gr. of the two forms is due to the variation in the sp. gr. of intermixtures of different proportions of the crystalline and amorphous sulphides, to the presence of occluded salts, and to the errors involved in the determination of the sp. gr. of very fine powders. There is no reliable evidence that cadmium sulphide crystallizes in more than one form ; the different colours of cadmium sulphide are due to differences in the size of the grains ; and G. Buchner and N. von Klobukoff's hypothesis is unnecessary.

The **crystals** of zinc sulphide are dimorphous, belonging either to the cubic system—sphalerite—or to the hexagonal system—wurtzite—and, according to C. Friedel, the axial ratio is $a : c = 1 : 0{\cdot}8175$. The crystals of zinc sulphide have been studied by A. Sadebeck, F. Becke, J. Nölting, P. Groth, G. vom Rath, A. Franzenau, C. A. Kenngott, C. Klein, A. Lacroix, C. Friedel, H. Förster, E. Döll, H. A. Miers, etc. Cadmium sulphide exhibits only the hexagonal form—greenockite—with the axial ratio $a : c = 1 : 0{\cdot}8109$. The crystals of cadmium sulphide have been studied by A. Breithaupt, N. von Kokscharoff, O. Mügge, R. P. Greg and W. G. Lettsom, M. F. Heddle, H. Viard, F. Rinne, G. T. Prior, E. Schüler, R. Schneider, W. Biltz, etc. E. T. Allen and J. L. Crenshaw stated : " We have crystallized cadmium sulphide by every method we could devise, and have obtained greenockite in every case " ; no cubic modification, analogous with zinc sulphide, has yet been prepared ; poorly developed twins of greenockite may represent the supposed monoclinic modification of cadmium sulphide. The cubic modification of zinc sulphide crystallizes in the form of distorted dodecahedrons at about 800° from molten sodium chloride ; as a mixture of dodecahedrons and tetrahedrons about 0·01 mm. diameter at 300° from a conc. soln. of sodium sulphide ; and in tetrahedrons alone when kept at 200° for 11 days in a similar soln. The hexagonal form of zinc sulphide appears in prismatic, hemimorphic crystals strongly striated

across the prism faces; in crystals tabular parallel to the base and modified by a different pyramid on each end; and the hardened amorphous globules from coherent masses of small doubly refracting grains of wurtzite—radial forms like schalen blendes may appear. Wurtzite prepared by sublimation may appear in slender needles, or stout prisms. The hexagonal crystals of artificial greenockite were prismatic, with parallel extinction. The sublimate contains filaments and needles, stubby prisms, and twins after $10\bar{1}1$, and after 2023. The **X-radiogram** and the space-lattice [9] of zinc sulphide have been previously considered (Fig. 78, **1**. 11, 8). That of sphalerite has been considered by W. H. and W. L. Bragg, and M. L. Huggins; and that of wurtzite, by W. L. Bragg, and M. L. Huggins. The latter also considered the relation of the space-lattices to the cleavages of these two forms. The crystals of cadmium sulphide and of wurtzite are isomorphous, and, like zincite, their symmetry is of the dihexagonal polar type. The axial ratio is nearly the same for all three compounds; $a:c$ for ZnO is 1 : 1·608, for ZnS, 1 : 1·635, and for CdS, 1 : 1·632. The close-packed structure has $a:c=1:1{\cdot}632$. In the zinc blende form of zinc sulphide the structure is cubic, and W. L. Bragg adds:

> In zinc oxide the zinc atoms are arranged on a face-centred cubic lattice, of side 5·41 A. The oxygen atoms are on a similar lattice, derived from the former by a movement of translation which brings each oxygen atom into the centre of four zinc atoms arranged on the corners of a regular tetrahedron. The trigonal axes in zinc blende are polar. If the structure of wurtzite is the same as that of zinc oxide, as would appear to be the case, then in the crystals, both of zinc blende and wurtzite, every atom of sulphur is surrounded by four atoms of zinc at the corners of a regular tetrahedron, and every atom of zinc by four sulphur atoms similarly arranged. The dimensions of the structures are also almost identical. In wurtzite, for example, the distance between neighbouring zinc atoms is 3·85 A., in zinc blende it is 3·83 A. The nearest approach of the atoms is 2·35 A. (R. N. Pease gave 2·41 A.). The arrangement of the planes parallel to the plane (0001) of wurtzite is the same as that of the planes (111) in zinc blende, the axis perpendicular to the planes being in each case polar.

W. P. Davey found that cadmium sulphide exhibits the tetrahedral hexagonal lattice with sides 4·16 A., and the nearest approach of the atoms 2·54 A. The subject has been studied by G. Ewald, M. L. Huggins, and B. Quarder. The passage from the amorphous to the crystalline state of zinc and cadmium sulphides has been studied by F. Haber.

The crystals of greenockite may exhibit a very faint **pleochroism,** because the ordinary ray is more strongly absorbed in the green than the extraordinary ray. In white light the pleochroism of single crystals of cadmium sulphide is not perceptible, but in thin twin crystals it is seen by contrast in the two parts. E. T. Allen and J. L. Crenshaw studied the triangular **corrosion figures** of sphalerite produced by zinc chloride, and they correlated the changes in the optical properties, volume, and energy content of crystals of sphalerite and wurtzite; and J. Beckenkamp has discussed the close crystallographic relationship. F. Becke, and J. J. Krenner studied the corrosion figures of zinc blende with soln. of alkali hydroxides or carbonates; and G. Wulff, the cleavage.

C. J. B. Karsten [10] gave 3·9235 for the **specific gravity** of zinc sulphide; the reported values for sphalerite or zinc blende range from F. A. Genth's 4·033 to C. Kuhlemann's 4·07. J. Joly found from 4·020 to 4·082 for zinc blende 15°/4°. E. Madelung and R. Fuchs gave 4·0904–4·0946 (0°) for zinc blende, and 4·0648 (0°) for wurtzite. E. T. Allen and J. L. Crenshaw gave 4·102 at 25° (water at 4° unity) for the sp. gr. of sphalerite, and 4·087 at 25°/4° for the sp. gr. of wurtzite, so that the sp. gr. of the two minerals of identical composition are nearly the same, but the sp. gr. of wurtzite is very slightly lower. They also found for ferruginous sphalerites:

	Sonora (Mexico).	Scotland.	Guipuzcoa (Spain).	Queensland.	Breitenbrunn (Saxony).
Per cent. iron	0·15	1·43	5·47	10·8	17·06
Sp. gr. 25°/4°	4·090	4·079	4·030	3·98	3·935
Sp. vol.	0·2444	0·2451	0·2481	0·2513	0·2541

E. Schüler gave 4·5 for the sp. gr. of artificial cadmium sulphide ; and for greenockite, C. J. B. Karsten gave 4·605 ; H. J. Brooke, 4·80 ; A. Breithaupt, 4·908 ; A. K. Christomanos, 4·77 ; A. Connell, 4·842 ; and A. Mourlot, 4·8. According to E. T. Allen and J. L. Crenshaw, the sp. gr. of a sample of greenockite with 0·086 per cent. of lead, and 0·002 per cent. of iron, was 4·820 at 25°/4°, and it is believed that most of the reported numbers are too high. The sp. gr. of the supposed polymerized forms of cadmium sulphide are indicated above. The **hardness** of zinc blende is given as varying from 3·5 to 4·0 ; of wurtzite, 3·0 to 4·0 ; and of greenockite, a little over 3. This subject was discussed by A. Reis and L. Zimmermann. R. Frankenheim, and A. Baumgartner and A. von Ettingshausen found a maximum hardness on the dodecahedral surface corresponding to the largest diagonal, and a minimum on the surface of the smallest diagonal of zinc blende. F. Exner, E. Pfaff, and G. Cesaro also studied the hardness of the crystals of zinc blende. E. Madelung and R. Fuchs gave for the **compressibility** of zinc blende $1{\cdot}28\times10^{-6}$ to $1{\cdot}29\times10^{-6}$, and for that of wurtzite $1{\cdot}34\times10^{-6}$ megabars per sq. cm. K. Försterling studied the elastic constants of zinc blende.

H. Kopp [11] measured the **coefficient of thermal expansion** of zinc blende, and found $0{\cdot}000036\pm0{\cdot}000002$ between 15° and 47° ; and for a black variety, $0{\cdot}000047\pm0{\cdot}000006$. H. Fizeau gave 0·00000670 at 40°, or at θ°, $0{\cdot}00000619+0{\cdot}0000001128\theta$. A. S. Herschel and G. A. Lebour found the **thermal conductivity** of zinc blende with 28 per cent. of quartz to be 0·08 C.G.S. unit. F. E. Neumann found the **specific heat** of different specimens of zinc blende to be 0·1132, 0·1148, 0·1156 ; H. V. Regnault, 0·12303 between 15° and 98° ; H. Kopp found a black variety to have the sp. ht. of 0·120 between 16° and 46° ; J. Joly, 0·1159 between 10° and 100° ; G. Lindner found 0·1146 at 100° ; 0·1153 at 200° ; 0·1162 at 300° ; and 0·1167 at 350°. K. Bornemann and O. Hengstenberg found the sp. ht. of zinc blende rises from 0·1249 at ordinary temp. to 0·1351 at 900°. The sp. ht. of the zinc-iron blendes suggest a reciprocal solubility of ferrous and zinc sulphides. Between 720° and 760°, the iron-zinc blendes show two transition points indicating allotropic forms. K. Försterling studied the sp. ht. of zinc blende.

According to E. T. Allen and J. L. Crenshaw,[12] when cadmium sulphide is heated, its colour becomes progressively darker, until, at about 800°–900°, it is dark red ; on cooling, the sulphide returns to its former colour. Amorphous cadmium sulphide crystallized in two days at 450°. According to J. Weber, when isotropic sphalerite is heated in a Bunsen's flame, and cooled quickly, it becomes anisotropic ; W. Biltz stated that when heated sphalerite changes to wurtzite without sublimation ; and F. Beijerinck transformed sphalerite into wurtzite by heat. E. T. Allen and J. L. Crenshaw found that an enantiotropic change occurs at the **transition temperature,** $1020°\pm5°$, when sphalerite or β-zinc sulphide changes to wurtzite or α-zinc sulphide. The former is stable below and the latter above the transition temp. ; nevertheless, both forms may be crystallized at comparatively low temp. from aq. soln. Zinc sulphide is very difficult to crystallize at temp. below 200°, and neither form of zinc sulphide has been obtained in the wet way by J. Weber or E. T. Allen and J. L. Crenshaw. The change from wurtzite to sphalerite is sluggish so that it is easy to cool the former to atm. temp. without any transformation ; it required 66 hrs. between 800° and 900° to change sphalerite entirely into wurtzite ; and it required 48 hrs. between 850° and 900°, and 40 hrs. between 850° and 950°. The presence of ferrous sulphide lowers the transition temp. ; thus :

Per cent. of iron . .	0·15	1·43	5·47	10·8	17·06
Transition temp. . .	1020°	998°	955°	919°	880°

Wurtzite changes into sphalerite more rapidly when heated in a bath of molten sodium chloride than when heated in vacuo, or in an atm. of hydrogen sulphide—there are also signs of the reaction $2NaCl+ZnS=Na_2S+ZnCl_2$. The accelerating influence of an acid on the transformation of wurtzite to sphalerite is illustrated by Fig. 48. G. Buchner, N. von Klobukoff, R. Lorenz, and F. Beijerinck have reported

crystalline forms of cadmium sulphide other than greenockite. The last-named mineral is the only natural crystalline form of cadmium sulphide. E. T. Allen and J. L. Crenshaw studied the heating curves of cadmium sulphide, and also the various modes of preparation in the quest for a second crystalline form, but the results were negative. R. Cussak stated that the **melting point** of zinc blende or sphalerite is 1049°, and K. Friedrich, about 1660°; but no other observer has been able to confirm this, although many have observed that the **sublimation temperature** or the temp. at which zinc sulphide volatilizes is near 1000°. Although cadmium and zinc sulphides sublime without melting, E. Tiede and A. Schleede found that zinc sulphide melts between 1800° and 1900° when heated under 100–150 atm. press. in an atm. of nitrogen, and the cold mass of wurtzite has a light greenish-yellow lustrous appearance; cadmium sulphide melts at about 1750° at 100 atm. press. The cold mass was a dark brownish-yellow lustrous solid. H. St. C. Deville and L. Troost stated that zinc blende does not volatilize at a white heat; T. Sidot, P. Hautefeuille, A. Mourlot, A. Ditte, A. Lodin, J. Percy, and K. Friedrich observed the slight volatility of the oxide, and C. Zenghelis stated that zinc sulphide is more volatile than the oxide. F. O. Doeltz and C. A. Graumann found that zinc blende and artificial zinc sulphide are but slightly volatile at 1000°, but copiously at 1200°; and, according to W. Biltz, zinc blende begins to sublime at 1178°±2°, and wurtzite, at 1185°±6°. E. T. Allen and J. L. Crenshaw observed no melting under any circumstances when zinc sulphide is heated at atm. press.; dipping a tube containing zinc sulphide quickly into a furnace at 1550° gave a negative result. H. Rose noted that cadmium sulphide cannot be heated in a stream of hydrogen without loss; H. N. Morse and J. White found that cadmium sulphide can be sublimed more readily than zinc sulphide, and that both sulphides sublime undecomposed when heated to redness, with their respective metals. The action is similar to the phenomenon observed with the oxides, and is not due, as first supposed, to dissociation, but is purely mechanical and occurs when powdered porcelain is used in place of the metals. W. Biltz found that sublimation occurs at 980°; and F. Damm and F. Krafft observed that rapid volatilization occurs in vacuo at 770°–780°. A. Colson said that cadmium sulphide dissociates at 600°. A. Heiduschka stated that cadmium sulphide does not alter when cooled to −186°.

According to M. Berthelot,[13] the heat of formation of zinc sulphide is (Zn, S) solid, 43·0 Cals., and, according to J. Thomsen, that of cadmium sulphide is 34·36 Cals. M. Berthelot also gave for one eq. of $Zn(C_2H_3O_2)_2$ in two litres of water and one eq. of H_2S in 10 litres of water, 1·81 Cals.; for dry $Zn(C_2H_3O_2)_2+H_2S_{gas}=2HC_2H_3O_{2gas}+ZnS+3·0$ Cals.; $ZnCl_{2soln.}+H_2S_{soln.}=2HCl_{aq.}+ZnS-0·2$ Cal.; $ZnSO_{4soln.}+H_2S_{soln.}=H_2SO_{4aq.}+ZnS-2·1$ Cals. According to J. Thomsen, the heat of the reaction between aq. soln. of zinc nitrate and hydrogen sulphide is −1·86 Cals., and for $Cd+S+nH_2O=CdS.H_2O+(n-1)H_2O+34·4$ Cals.

The **index of refraction** of yellow zinc blende from Picos de Europa (Santander, Spain) was found by A. des Cloizeaux[14] to be $\mu=2·341$ for Li-light, and $\mu=2·369$ for Na-light, at 15°. W. Ramsay found $\mu=2·34165$ for Li-light, $\mu=2·36923$ for Na-light, and $\mu=2·40069$ for Tl-light. E. T. Allen, J. L. Crenshaw, and H. E. Merwin found for pure sphalerite, $\mu=2·3682$ for Na-light, and $\mu=2·3983\pm0·0002$ for Tl-light; for wurtzite with the ordinary ray $\omega=2·33$, and with the extraordinary ray $\epsilon=2·35$; while the amorphous jelly may give $\mu=2·18$–$2·25$. The development of double refraction is the only conclusive evidence of the change from sphalerite to wurtzite by heat. The wurtzite begins developing at more than one point, and in different orientations, and the resulting structure is an intergrowth of lamellæ of wurtzite, and, as shown by P. Hautefeuille, each lamella has its principal axis parallel to one of the trigonal axes of the sphalerite grain. The double refraction of a grain thus transformed will be conditioned by the development of the four possible sets of lamellæ. J. Beckenkamp has considered that lamellæ of wurtzite may develop parallel to the trapezohedron of sphalerite. Such lamellæ would outcrop on a cleavage face parallel or normal to cleavages or bisecting the acute angle

between cleavage surfaces. All of the outcropping planes would be oblique to cleavage planes. E. T. Allen, J. L. Crenshaw, and H. E. Merwin observed no lamellæ of this kind. The refractive indices of greenockite were $\epsilon=2{\cdot}447$ and $\omega=2{\cdot}425$ for Li-light, and for Na-light $\epsilon=2{\cdot}529$ and $\omega=2{\cdot}506$. The refractive index of sphalerite is raised when ferrous sulphide is present, and that of greenockite artificially prepared is lowered by adsorbed impurities :

Per cent. FeS . .	0·2	8·6	17·0	28·2
Sp. gr. D . . .	4·090	4·023	3·980	3·935
μ for Li-light . .	2·34	2·36	2·38	2·395
μ for Na-light . .	2·37	2·40	2·43	2·47
$(\mu-1)/D$ for Na-light .	0·335	0·348	0·358	0·373

G. Horn, and W. Voigt gave for a pale yellow blende from Santander, and a black blende from St. Christoph (Breitenbrunn, Saxony), the refractive index μ, and the **index of absorption,** k :

		C-line.	D-line.	E-line.	F-line.	G-line.
Santander	μ . .	2·397	2·421	2·439	2·472	2·528
	k . .	0·0221	0·0194	0·0284	0·0265	0·0313
Breitenbrunn	μ . .	2·434	2·437	2·464	2·471	2·559
	k . .	0·0429	0·0529	0·0571	0·0623	0·0942

E. T. Allen, J. L. Crenshaw, and H. E. Merwin observed with a sample of sphalerite from Sonora (Mexico), and a sample of pure greenockite :

$\lambda=$	420	434	486	535	589	630	671	760$\mu\mu$
$\mu=$	2·517	2·493	2·436	2·399	2·369	2·353	2·340	2·320

H Becquerel and M. Baille made observations on this subject. S. y C. del Rio Calderon found for Na-light :

	20°	60°	100°	140°	180°	200°
μ . .	2·369	2·373	2·378	2·385	2·393	2·398

Wurtzite is optically positive ; and the **double refraction** is feeble—this subject was investigated by A. des Cloizeaux, C. Friedel, J. L. C. Schröder van der Kolk, L. Bertrand, E. Mallard, J. Nölting, etc. W. Phillips, and A. Madelung found greenockite to be optically positive, and the double refraction feeble. D. Brewster showed that the crystals of zinc blende are optically anomalous, and the subject was investigated by P. Hautefeuille, J. Hirschwald, R. Brauns, E. Mallard, L. Bertrand, H. Rose, and F. Quiroga. For wurtzite, the double refraction $\epsilon-\omega$ is 0·019 for Li-light and 0·020 for Na-light ; and for greenockite these values are respectively 0·025 and 0·023. The curves for the variation of the refractive index of greenockite with the wave-length gradually approach one another since the refractive index ω increases more rapidly than ϵ ; there is therefore a change in the optical sign at the point of intersection of the curves when $\mu=2{\cdot}6$ and $\lambda=525\mu\mu$ (extrapolation). The light absorption of greenockite was found by E. T. Allen, J. L. Crenshaw, and H. E. Merwin to be very small for ω below a wave-length $519\mu\mu$, and from 517 to $511\mu\mu$ it increases to near complete opacity ; for ϵ, absorption begins near $512\mu\mu$, and increases to $506\mu\mu$. W. W. Coblentz measured the **infra-red transmission spectrum** for sphalerite and found the crystals to be transparent from 5 to 12μ, with slight depressions in the curve at 1·6, 11·2, and $13{\cdot}2\mu$; there is a wide band from 2·7 to $3{\cdot}3\mu$, and complete opacity beyond 15μ. The **infra-red reflection spectrum** was also studied by W. W. Coblentz, and by T. Liebisch and H. Rubens.

E. L. Nichols and D. T. Wilbur [15] found that purified zinc sulphide, like calcium oxide, exhibits **flame luminescence.** Highly purified zinc sulphide—wurtzite or sphalerite—either shows no **phosphorescence** or it phosphoresces very slightly. E. MacDougall, A. W. Stewart, and R. Wright showed that highly purified zinc sulphide can be obtained in a condition which enables it to phosphoresce ; the amorphous sulphide does not phosphoresce, nor does the wholly crystalline sulphide phosphoresce so well as a semi-crystalline sulphide. The fused sulphide was found

by E. Tiede and A. Schleede to be strongly phosphorescent. The temp. to which the zinc sulphide has been heated and the time of heating have the greatest influence on the phosphorescence. W. Molthan found the dielectric constant is increased in light. According to E. Tiede and A. Schleede, the effect of a flux in inducing the phosphorescence of zinc sulphide is not due to the formation of a definite crystalline form, but rather to the lowering of the m.p. The presence of certain impurities—*e.g.* iron—inhibits the phosphorescence; others—*e.g.* manganese—alter the tint. The presence of a chloride favours the phosphorescence, so that, as E. MacDougall and co-workers showed, samples of the sulphide made from zinc salts not containing chlorides do not phosphoresce so brilliantly as those produced in the presence of chlorides; presumably some chloride is adsorbed as an impurity not removable by washing—*vide* the phosphorescence of the sulphides of the alkaline earths. As a rule, natural zinc blende does not phosphoresce. When the isolated mineral is examined in a darkened room, S. R. Mourelo found the phosphorescence is more intense with diffused daylight than with sunlight; W. Trenkle found the **photo-luminescence** to be favoured by concentrating the rays from an arc-light with a lens. K. A. Hofmann and W. Ducca found that the luminescence is evoked by exposure to daylight, the incandescent light, arc-light, Becquerel's rays, and cathode rays, and H. Zahn, B. Gudden and R. Pohl, that the phosphorescence can be excited in powerful electric fields—say 3000 volts per cm. M. Curie studied the effect of the red and infra-red rays on phosphorescent zinc sulphide. He observed that the sulphur atoms of the X-radiogram were not influenced—it was assumed that if these atoms were agitated by light, there would be a diminished intensity in the reflected X-rays. J. L. Pech found samples of zinc sulphide which phosphoresced in the ultra-violet, but not in the infra-red; and L. B. Löb and L. Schmiedeskamp noted a decrease in the intensity of the phosphorescence as the time of exposure to ultra-violet light increased. W. Crookes, H. Becquerel, T. Tommasina, P. Curie and A. Debierne, H. Grüne, and A. A. Guntz studied the phosphorescence which zinc blende produces when exposed to radium radiations. The phosphorescence is also evoked by exposure to the spark discharge; the X-rays and the canal rays are also effective. According to H. A. Bumstead, the scintillations of zinc blende are produced by the secondary rays from lead. According to H. Becquerel and T. Tommasina, the α-rays produce a scintillating phosphorescence which rapidly vanishes. According to J. Elster and H. Geitel, the phenomenon is produced by the radio-active emanation from the earth, and by air which has been passed over thorium hydroxide. According to H. Becquerel, the scintillation is not produced by ionization, but by the impact of the α-particles of radium, and is obtained by rubbing zinc blende between two glass plates, *i.e.* the flash is due to the cleavage of the crystals by the bombardment with α-corpuscles, *i.e.* of triboluminescence. W. Crookes also regarded the flash as an effect of the impact of an α-particle. R. W. Wood found the duration of the flash is between 15×10^{-5} and 20×10^{-5} secs. and is shorter than the triboluminescent flash so that the two phenomena are not closely related. Only a small percentage of the sulphide phosphoresces under the α-rays. He assumes that the flash occurs only when an electron strikes a molecule of the impurity because the number of α-particles emitted by radium far exceeds the number of flashes in the spinthariscope. E. Wiedemann and G. C. Schmidt assume that the active substance is dissociated during excitation, and that the recombination of the products of dissociation is accompanied by the emission of light. Mixtures of radium with zinc sulphide emit a greenish-yellow light due to the bombardment of the zinc sulphide crystals by the α-particles from the radium. The mixture has been used for permanently illuminating keyholes, the hands of clocks and watches, etc., so that these may be readily seen in the dark. C. Henry found phosphorescent zinc sulphide enhances the photographic activity of X-rays. H. Herszfinkiel and L. Wertenstein have shown that the range of the α-particles in zinc sulphide is of the order of some hundredths of a millimetre. R. Pohl and co-workers studied the dielectric constant of phosphorescent zinc sulphide.

F. Giesel and J. Zanneck found the phosphorescence of Sidot's blende exceeds that of all other known substances. According to C. Baskerville and L. B. Lockhart, Sidot's blende phosphoresces under the influence of the gaseous emanations obtained when some rare-earth minerals are heated, but purified preparations of uranium or thorium give no results. According to A. S. Eakle and W. T. Sharwood, zinc blendes from Kapnik (Hungary), Mariposa (California), Eureka (Nevada), Utegrube (Rico), etc., are phosphorescent. These blendes lose the quality superficially when heated to 1000°, and when roasted, this property is destroyed. Artificial or natural zinc blende which has been heated in a stream of hydrogen acquires the property of phosphorescing, and A. Verneuil suggests that hydrogen possibly produces a lower zinc sulphide which is the cause of the phenomenon.

T. L. Phipson observed that a white pigment prepared by precipitating zinc sulphide from a soln. of zinc sulphate by barium sulphide, appeared black all day, and again became white at night. The powder exposed to sunlight became fawn-coloured, brown, and finally a dark slate colour in about 20 mins. If the darkened powder be placed in darkness, it becomes white again in $2\frac{1}{2}$ to 3 hrs. The power of alternately darkening and whitening was lost in a few days, although specimens of the powder have retained the property for months or years. T. L. Phipson wrongly assumed that the blackening is due to the presence of an element sensitive to light and which he called *actinium*. J. Cawley assumed that some zinc oxide is formed during the calcination, and that this reacts with zinc sulphide, forming zinc and sulphur dioxide which blackens the mass. This agrees with the fact that (i) the sensitiveness to light is greater when the sulphide is moist than when it is dry, and (ii) the presence of magnesia retards the blackening.

Zinc sulphide is sometimes substituted for zinc-white as a pigment, and it has rather a greater covering power. The sulphide is made by bringing together the vapours of the two elements, and collecting the product in settling chambers from which air is excluded. J. Cawley, and C. Clerc and A. Nihoul also described manufacturing processes. As a rule, the sulphide is not used alone, but is mixed with barium sulphate —C. F. Claus. Hot soln. of barium sulphide and zinc sulphate are mixed, and the washed precipitate is dried, mixed with ammonium chloride, heated to redness, and quenched in water. The product is used as a pigment under the trade name *lithophone*. An analogous mixture of zinc sulphide and calcium sulphate furnishes *sulphophone*—C. R. P. Steinau. Lithophone turns grey in direct sunlight. If mixed with lead or copper compounds, the paint blackens owing to the formation of black lead or copper sulphide. Zinc sulphide and lithophone are coloured grey by exposure to light or by heating them to 60°–70°. W. J. O'Brien attributed the coloration to the decomposition of the sulphide into sulphur and metal, but Y. Nishizawa could detect no free sulphur in a discoloured specimen, and he attributes the coloration to the polymerization of the sulphide. He found the discoloration is promoted by magnesium, zinc, or calcium chloride or sulphate; and inhibited by polyhydric alcohols, sugars, starch, oxalic acid, tartrates, etc.

From the discussion on the preparation it follows that the phosphorescence of zinc sulphide is dependent on the presence of small traces of certain impurities. According to A. Verneuil, and P. Lenard and V. Klatt, the presence of 0·001 part of zinc sulphide changes the colour but not the intensity of the phosphorescence of calcium sulphide. C. A. Pierce studied the decrease in phosphorescence produced at temp. rising from 15° to 300°. E. Wiedemann and G. C. Schmidt say that the phosphorescence of Sidot's blende is retained up to 500°, and the glow is gradually extinguished. C. Henry found the rate of decay of the phosphorescence could be represented by the rule $I=I_0e^{-at}$, where the intensity of the light at the time t is represented by I; and I_0 is the initial intensity; a and e are constants. E. Becquerel gave the more complex formula $I^{0\cdot5936}(27\cdot18+t)=1647\cdot5$. R. Tomaschek examined the effect of different modes of preparation on the spectrum of the phosphorescent light.

L. Clémandot found that the phosphorescence of zinc blende is excited mainly by the rays more refrangible than the F-ray. A. Dahms showed that an exposure to the ultra-red rays rapidly extinguishes the phosphorescence of zinc blende. R. Danneberg found that wurtzite phosphoresces with light of short wave-length,

and the luminosity is extinguished by heat rays. The photoluminescence decays more slowly than the cathodoluminescence. The phosphorescence is most intense when evoked by exposure to the violet and blue rays ; the green rays produce a feeble phosphorescence ; and the rays from orange to red produce no result. According to E. L. Nichols and E. Merritt, the luminescence spectrum shows two well-defined bands at $\lambda=0{\cdot}507\mu$ and $\lambda=0{\cdot}432\mu$; the violet band is produced by the ultra-violet part of the arc-light between iron or zinc electrodes ; the green band is most rapidly produced by the violet band of the arc between carbon electrodes ; and both bands are produced by X-rays, and by ultra-violet light. The phosphorescence of Sidot's blende does not follow Stokes' law. The full effect of the exciting light is produced in three seconds. The intense violet light is of short duration and dies out in one or two tenths of a second ; while the fainter green light is of long duration, and it can be detected several hours after excitation has ceased. E. Lenard said that the blackening which occurs when zinc sulphide is exposed to light is due to a film of finely divided zinc ; the blackening does not occur in the absence of moisture.

According to W. Trenkle, zinc blende exhibits **triboluminescence** when triturated, compressed, or hammered. According to W. S. Andrews, zinc sulphide prepared in the following manner emits sparks of yellow light when scratched with a knife :

> Triturate a mixture of 70 parts of zinc carbonate with 30 of flowers of sulphur to a thick cream with distilled water in which a little manganese sulphate has been dissolved. Dry the mass at a gentle heat, and pack the powder in a porcelain or plumbago crucible and heat to bright redness for 20 mins.

The sparks do not ignite inflammable vapours. A. A. Guntz made some observations on this subject. The phenomenon was first reported by F. Hofmann in 1750, the effect may be really **thermoluminescence** due to the heat developed by friction. The thermoluminescence is brilliant but rapidly decays. According to A. S. Eakle and W. T. Sharwood, zinc blende from Mariposa (California) exhibits a strong triboluminescence, and the ore is a mixture of barytes, and zinc blende with sulphides of lead, antimony, and copper. E. Wiedemann and G. S. Schmidt found many mixtures of salts are triboluminescent—*e.g.* isomorphous mixtures of zinc sulphide with the sulphides of the alkaline earths. H. Grüne refers the triboluminescence of natural blende to the presence of traces of manganese. According to H. Baumhauer, Sidot's blende luminesces if breathed upon, if exposed to steam, or if treated with cold or hot water ; and M. Seddig found that it luminesces when cooled. According to R. Schenck and F. Mihr, Sidot's blende begins to luminesce when exposed to ozonized air, and F. Richerz and R. Schenck say that this is not due to oxidation. L. Vanino found that a photographic plate wrapped in paper is blackened by zinc sulphide in consequence of the reducing action of hydrogen-sulphide vapour—if surrounded by celluloid, transparent to Becquerel's rays, the blackening does not occur.

B. Pelletier [16] found zinc sulphide to be a good conductor of electricity, but, added M. Kiliani, only when the sulphide is impure. F. Beijerinck found the **electrical conductivity** even of the dark varieties of zinc blende is nil ; wurtzite and greenockite conduct feebly at ordinary temp., but the conductivity increases as the temp. is raised—the conductivity, according to M. Kiliani, is due to polarization currents and infra-crystalline separations of zinc. G. Karsten found that cadmium sulphide prepared in the dry way conducts electricity feebly, but if prepared in the wet way, it is a non-conductor. F. Beijerinck found yellow greenockite is a non-conductor, while the orange sulphide is a conductor. R. Bädecker studied the conductivity of thin films of cadmium sulphide. G. Tammann measured the potential of zinc blende against the normal hydrogen electrode, and showed that in aq. soln. there is an exchange of ions. B. Gudden and R. Pohl found that the electrical conductivity of zinc and cadmium sulphides is augmented in light. H. Zahn measured the rectifying effect of zinc blende on alternating currents. Crystals of

zinc blende were found by C. Friedel and P. Curie to exhibit **pyroelectricity** such that the tetrahedral surface and the corners were oppositely charged; J. and P. Curie observed that the crystals exhibited **piezoelectricity** where the tetrahedral surfaces were negatively charged, and the corners were positively charged. W. Schmidt found the **dielectric constant** of zinc blende to be 75; and the electrical index of refraction 7·85. B. Gudden and R. Pohl observed that the dielectric constant is increased under the influence of light; and that the increase with monochromatic light is less rapid than the increase in the intensity of light. According to P. Curie, zinc blende is a dielectric to which the law of the superposition of e.m.f. does not apply, probably because of liquid inclusions. H. Becquerel said that the **magnetic rotation** of the plane of polarization of zinc blende is seventeen times the value for water. W. Voigt and S. Kinoshita measured the **magnetic susceptibility** of zinc blende. O. Knoblauch, and B. Gudden and R. Pohl showed that zinc blende, greenockite, or cadmium sulphide exhibit the **photoelectric effect.** W. Biltz found that colloidal zinc or cadmium sulphide suspended in water, under the influence of an electric current, migrated to the cathode. The coagulation of colloidal cadmium or zinc sulphide in sunlight was observed by P. B. Ganguly and N. R. Dhar.

The chemical properties of zinc and cadmium sulphides.—According to K. Hüttner,[17] a specimen of zinc blende at 800° to 850° gave off 1·6 times its vol. of **occluded gases**—hydrogen, 14·6 per cent.; carbon monoxide, 75·6 per cent.; and nitrogen, 9·8 per cent., but no rare gases. According to A. Mourlot, zinc sulphide is not decomposed when heated even in the electric-arc furnace provided air be absent; and W. Fränkel observed no change when zinc blende is heated to 1300° in an atm. of **nitrogen**. H. St. C. Deville and L. Troost, H. N. Morse and J. White, and A. Verneuil found that zinc or cadmium sulphide sublimes when heated in a stream of **hydrogen.** P. Berthier found that hydrogen has no action on zinc sulphide. E. Pollacci regarded zinc sulphide as a member of those sulphides difficult to oxidize in **air.** Cadmium sulphide is moderately oxidizable in air; F. Janda said that zinc blende oxidizes in air faster than galena; and A. Kunze and K. Danziger, that it oxidizes in moist air between 50° and 300° more slowly than iron pyrites. R. Wagner found that zinc blende slowly decomposes in moist air with the evolution of hydrogen sulphide, and J. Böhm stated that it gives off hydrogen sulphide between 150° and 200°. A. Richardson found that cadmium yellow becomes paler when exposed to light in moist air owing to its oxidation to the sulphate, but in dry air it is not changed.

When zinc sulphide is heated to redness in air, zinc oxide and zinc sulphate are formed. The roasting proceeds with difficulty, and, as F. Janda, J. Sachse and E. Richter, and L. Bemelmans have shown, the powder to be roasted should be in a finely divided state. The roasting of zinc sulphide in an atm. of **oxygen** proceeds: $2ZnS+3O_2 \rightarrow 2ZnO+2SO_2$; the reverse reaction has not been observed. There is an unstable equilibrium between sulphur dioxide and oxygen in the presence of the catalytic agents: $SO_2+O_2 \rightleftharpoons 2SO_3$; and the sulphur trioxide reacts with the oxide: $ZnO+SO_3 \rightleftharpoons ZnSO_4$. There is then a definite press. of sulphur trioxide corresponding with every temp.—*vide* sulphur trioxide. L. and P. Wöhler and W. Plüddemann give for the dissociation press. of zinc sulphate in mm. of mercury:

	675°	690°	720°	750°	775°	800°
Press.	5	6	24	61	112	189

When the temp. of the roasting sulphide rises to bright redness, the sulphate is decomposed; according to H. O. Hofman, a basic sulphate is formed, and at a white heat zinc oxide results. K. Friedrich found that sulphur dioxide can be detected at 40°, and the sulphide begins to glow in oxygen at 662° to 775°. J. W. Richards has calculated a theoretical temp. from the heats of formation of the reacting substances. R. Hasenclever showed that the best temp. for roasting zinc sulphide is about 960°, and the resulting zinc oxide should not be exposed to the action of carbon monoxide, or losses will occur through the reduction and volatilization of

zinc. E. Jensch found about two per cent. of sulphide-sulphur remained in roasted blende, and E. Orgler stated that well-roasted blende should not contain over 0·25 per cent. of sulphide-sulphur. V. Lepiarcyzk converted pure zinc sulphide wholly into the oxide by roasting, but with blende containing lime, calcium sulphate was formed. F. Kellermann, E. Prost, F. A. Thum, C. Ritter, E. Schuchard, E. Schütz, C. F. Plattner, F. Janda, A. Voigt, H. Brandhorst, H. Pommerenke, and P. Truchot, have studied the roasting of blende. H. O. Hofman found ferruginous blendes more difficult to roast than blendes containing less iron, and the yield of sulphate is higher; he did not find it possible to convert more than 9 per cent. of a raw blende into sulphate by roasting. E. Prost and E. Lecocq studied the roasting of fluoriferous blendes; C. Sander, argentiferous blendes; W. Mostowitsch, and C. Sander, barytiferous blendes; and G. Waring, J. E. Williams, E. Orgler, and V. Lindt, calcareous blendes. J. C. Clancy and L. W. Marsland shortened the time of roasting by mixing the blende with lead sulphate. A. Helbronner and W. Rudolfs state that certain bacteria, described by J. G. Lipman and co-workers, have been found which are capable of converting blende into zinc sulphate, and that the solubility of the product does not prevent the further action of the bacteria. The oxidation is favoured by the presence of sulphur, and under such conditions the bacteria can convert the native silicate and carbonate into sulphate. If lead sulphide is present, only the zinc sulphide is attacked, and the two metals can thus be separated.

According to A. Mailfert,[18] **ozone** converts zinc or cadmium sulphide into the sulphate. When zinc sulphide is heated in **water** vapour, H. V. Regnault found that zinc oxide and hydrogen sulphide are formed, the decomposition is incomplete except at a very high temp. in a porcelain tube, and the zinc oxide is then deposited in small silky masses in that part of the tube from which the steam escaped; similar remarks apply to cadmium sulphide. From the electrical conductivity determinations, O. Weigel found for the solubility of zinc blende from Santander, $6{\cdot}65\times10^{-6}$ mol per litre; for artificial crystals, $5{\cdot}0\times10^{-6}$ and $8{\cdot}0\times10^{-6}$ mol per litre; for wurtzite, $28{\cdot}82\times10^{-6}$ mol per litre; for greenockite, $8{\cdot}99\times10^{-6}$ mol per litre; and for precipitated zinc and cadmium sulphides, respectively $70{\cdot}60\times10^{-6}$ and $9{\cdot}00\times10^{-6}$ mol per litre; L. Bruner and J. Zawadsky, $5{\cdot}0\times10^{-26}$ or $8{\cdot}0\times10^{-26}$ mol per litre for the alleged α-ZnS, and $1{\cdot}1\times10^{-24}$ mol per litre for β-ZnS. W. Biltz found from ultra-microscopic observations that the solubility of cadmium sulphide is $6{\cdot}6\times10^{-6}$ mol per litre at 16° to 18°.

Cold **chlorine** gas, or chlorine water, has very little action on zinc sulphide, but above 30° zinc and sulphur chlorides are formed: $2ZnS+3Cl_2=2ZnCl_2+S_2Cl_2$; W. Borchers and A. Dorsemagen[19] stated that the action begins in the wet way at 30°–40° with the liberation of sulphur, and E. A. Ashcroft said the reaction begins above 600°: $ZnS+Cl_2=ZnCl_2+S$. E. Schäfer observed no reaction when zinc blende is heated to dull redness with chlorine or **bromine.** E. Filhol and J. Melliès found that when heated with **iodine** in a sealed tube at 200°, zinc sulphide is completely transformed into zinc iodide. H. V. Regnault found zinc blende to be soluble in hot conc. **hydrochloric acid,** with the evolution of hydrogen sulphide—*vide supra,* preparation of zinc sulphide. F. Stromeyer found that cadmium sulphide is sparingly soluble in hot dil. hydrochloric acid, but easily soluble in cold conc. acid; O. Follenius and W. Spring made a similar observation. J. B. Meyer converted the sulphide into chloride by heating it in a stream of hydrogen chloride. L. E. Rivot, F. S. Beudant, and P. A. Daguin found that powdered zinc sulphide is completely dissolved when digested for some hours with a hot conc. soln. of potassium hydroxide sat. with chlorine—**alkali hypochlorite;** S. S. Sadtler also found it to be dissolved by an alkaline soln. of sodium hypochlorite; and J. Lemberg by an **alkali hypobromite** soln. F. Repiton found zinc sulphide decomposes **starch iodide.** A. S. Cushman found that unlike copper sulphide cadmium sulphide is soluble in a hydrochloric acid soln. of **sodium chloride.** The chloridized roasting of pure blende has been previously discussed.

According to F. Wöhler and co-workers,[20] **sulphur dioxide** reacts very slowly with zinc blende, forming sulphur $2ZnS+SO_2=2ZnO+3S$; the film of basic sulphide simultaneously formed protects the sulphide from the sulphur dioxide. Zinc blende was found by E. F. Smith to be completely decomposed by the vapour of **sulphur chloride**, S_2Cl_2; and N. A. Orloff, and H. Feigel found that when dry zinc or cadmium sulphide is shaken with a benzene soln. of sulphur chloride, S_2Cl_2, and the liquid decanted from the greenish-black lumps, and warmed to 70°, almost pure sulphur is deposited. They also found that similar results are obtained by digesting dry cadmium sulphide with benzene, carbon disulphide, or toluene soln. of sulphur chloride. E. Paterno and A. Mazzuchelli found that **sulphur bromide,** S_2Br_2, acts similarly, while the so-called **sulphur iodide,** S_2I_2, is inactive. H. St. C. Deville and L. Troost found that zinc sulphide does not sublime in a stream of **hydrogen sulphide.** According to A. Villiers, amorphous zinc sulphide dissolves in an aq. soln. of hydrogen sulphide, but the crystalline sulphide does not dissolve in that menstruum. G F. Becker found that zinc sulphide is soluble in a cold soln. of **sodium sulphide,** Na_2S, without the development of gas; almost insoluble in a cold, but a little more soluble in a hot soln. of **sodium hydrosulphide,** NaSH; and soluble in a soln. of sodium carbonate partially sat. with hydrogen sulphide. P. Berthier stated that zinc sulphide combines with most of the metal sulphides—iron, antimony, lead—though with difficulty, and the combinations which are formed do not readily fuse. L. L. de Koninck could find no evidence of a compound of zinc and ferrous sulphides. R. Schindler prepared **potassium zinc sulphide,** $K_2S.3ZnS$, or $K_2Zn_3S_4$, by dissolving zinc sulphide in a molten mixture of sulphur and potassium carbonate and, after 10 mins.' fusion, washing the cold mass with water. The small colourless crystals are stable in air; and they are not changed when heated red hot in the absence of air, or hydrogen. They do not give potassium sulphide with hot or cold water, but the moist crystals exposed to air, slowly form potassium thiosulphate. They are readily decomposed by mineral acids; with silver nitrate, they form **silver zinc sulphide,** $3ZnS.Ag_2S$; and with cupric sulphate, they form **cupric zinc sulphide,** $CuS.3ZnS$; but they do not react with mercuric chloride, lead nitrate, or thallium sulphate. Mixtures of zinc sulphide and **cuprous sulphide** do not show any eutectic structure, and only a single branch of the f.p. curve could be observed, the eutectic point, if present, lying close to the f.p. of cuprous sulphide. Mixtures of the **sulphide of silver** and that of zinc form a eutectic containing 3 per cent. ZnS and solidifying at 800°. R. Schindler also made **sodium zinc sulphide,** $Na_2S.3ZnS$, in an analogous manner. J. Milbauer prepared a **potassium cadmium sulphide** by melting cadmium oxide with potassium thiosulphate; but not the corresponding **sodium cadmium sulphide,** although R. Schneider prepared the latter by fusing cadmium sulphide with sodium carbonate and sulphur; the yellow crystalline powder remaining after washing with dil. alcohol had the composition $Na_2Cd_3S_4$, or $Na_2S.3CdS$.

A. Gueront found that zinc or cadmium sulphide is slightly soluble in an aq. soln. of **sulphur dioxide,** forming a thiosulphate; P. Berthier found freshly precipitated zinc sulphide dissolves in sulphurous acid. A. Rosentiehl noted that zinc chloride is formed when sulphur dioxide is passed into dil. hydrochloric acid holding zinc sulphide in suspension. According to H. V. Regnault, and M. Berthelot, zinc sulphide is largely decomposed by evaporation with conc. **sulphuric acid.** S. Glixelli found that the so-called β-ZnS is 4·6 times as soluble as α-ZnS in dil. sulphuric acid; he also found at 25° with N-H_2SO_4, 10 c.c. of a soln. of zinc blende from Santander contained 0·00059 grm. of zinc; with α-ZnS, precipitated at ordinary temp. the soln. contained 0·0025 grm. Zn; and when precipitated at 0°, 0·018 grm. Zn; the soln. of β-ZnS, precipitated at ordinary temp., contained 0·010 grm. Zn; and precipitated at 0°, 0·0316 grm. Zn when the sulphide was fresh, and 0·016 grm. of Zn when 5 days old—*vide supra*, preparation of zinc sulphide. A. W. Hofmann stated that cadmium sulphide is soluble in boiling $\frac{1}{3}N$-H_2SO_4, and O. Follenius, in boiling dil. sulphuric acid. R. Meldrum stated that cadmium sulphide is insoluble

in sulphuric acid. According to E. Jannettaz, when heated with **potassium hydrosulphate,** $KHSO_4$, zinc blende gives a little hydrogen sulphide.

H. W. F. Wackenroder [21] stated that cadmium sulphide is very sparingly soluble in aq. **ammonia.** H. Brandhorst found zinc blende is soluble in a boiling soln. of **ammonium acetate** with the separation of sulphur. C. R. Fresenius, and A. Ditte found **ammonium sulphide** dissolves marked quantities of cadmium sulphide, and a soln. of an **alkali sulphide** dissolves less, but E. Donath and J. Mayrhofer, and C. R. Fresenius added that the solubility is so small as to be of negligible importance in analysis. G. P. Baxter and M. A. Hines found cadmium sulphide to be appreciably soluble in a soln. of **ammonium chloride,** and P. de Clermont found both cadmium and zinc sulphides to be soluble in a boiling soln. of ammonium chloride. Zinc sulphide is soluble in weak mineral acids, best in **nitric acid.** H. V. Regnault, for example, stated that it dissolves in nitric acid with the separation of sulphur. W. Meissner, and O. Follenius, found cadmium sulphide to be readily soluble in nitric acid. J. Percy found that zinc sulphide is energetically oxidized when heated with an **alkali nitrate,** forming zinc oxide and alkali sulphate.

According to J. Percy,[22] and P. Berthier, when zinc sulphide is heated with **carbon,** or in a carbon-lined crucible, it volatilizes completely, leaving behind ferrous sulphide, if it contains iron ; he added that the zinc sulphide is probably decomposed with the formation of carbon disulphide. According to F. Janda, zinc sulphide is reduced with great difficulty by carbon. H. Moissan found that zinc sulphide is reduced by carbon in the electric arc furnace. W. Fränkel heated zinc blende mixed with 10 per cent. of carbon in a porcelain boat in a quartz tube ; between 1300° and 1350°, the porcelain and quartz were attacked, and the composition of the condensate was *zinc thiosilicate*, ZnSSi, with traces of carbon disulphide in the evolved gases. V. Lindt, and V. Lepiarczyk concluded that the reaction between carbon and zinc sulphide is to be symbolized : $2ZnS+C=2Zn+CS_2$. This reaction between carbon and the metal sulphides was indicated by C. Stölzel in 1863. When zinc sulphide is heated with carbon and lime, metallic zinc and calcium sulphide are formed ; the reaction is incomplete and depends on the temp. J. Percy found that zinc sulphide, even at a red heat, is not affected by dry **carbon dioxide.** N. D. Costeanu observed no action at 600°, but at 750° there are indications of a reaction : $ZnS+CO_2=CO+ZnO+S$; with cadmium sulphide dissociation begins at about 600°, but the gas exerts no chemical action. According to P. Berthier, when zinc sulphide is fused with **alkali carbonates** at a red heat, a mixture of zinc oxide, zinc sulphate, and alkaline sulphide is formed. Freshly precipitated zinc sulphide was found by H. W. F. Wackenroder to be slightly soluble in a large excess of **acetic acid ;** and R. Meldrum said that cadmium sulphide is insoluble in acetic acid. W. Fränkel found that when zinc sulphide is mixed with **silicon,** and heated in a quartz boat in a quartz tube, distillation begins at 1150°, and ZnSSi is formed as in the case of carbon in the porcelain boat. O. Stutzer has studied the action of zinc blende on natural **silicates.**

According to J Percy,[23] **iron** decomposes zinc sulphide at a bright red heat, forming ferrous sulphide and the vapour of zinc ; C. A. Graumann found the reaction with finely divided iron : $ZnS+Fe=FeS+Zn$, is practically complete at 1300°. J. Percy continued : the reduction with **tin** is more or less incomplete ; **antimony** does not reduce zinc sulphide even at a high temp. ; **lead** reduces zinc sulphide very imperfectly ; and **copper** reduces zinc sulphide at a high temp., forming a regulus, and the proportion of zinc remaining alloyed with the copper depends on the temp. and the duration of the operation.

E. F. Smith found that powdered zinc blende is oxidized when suspended in molten **potassium hydroxide** with the containing nickel dish as anode. Cadmium sulphide, said C. R. Fresenius, is quite insoluble in alkali lye. S. H. Walton and H. A. Scholz found that **sodium peroxide** with a trace of potassium persulphate is a convenient medium for opening up zinc blende for analysis. According to P. Berthier, zinc sulphide and **calcium oxide** decompose one another only in the

presence of carbon ; but J. Percy obtained some decomposition when lime and zinc sulphide were heated together ; and E. Prost found that eq. quantities of lime and zinc sulphide react at 1200°, but with 75 per cent. excess of lime, decomposition is complete at 1250°. P. Berthier stated that zinc oxide does not decompose zinc sulphide, but the two components form a **zinc oxysulphide** which is fusible at high temp. C. Kersten reported a crystalline incrustation, ZnO.4ZnS, on a Freiburg furnace, but J. J. Berzelius pointed out that the analysis of C. Kersten did not justify the proposed formula. The mineral *voltzite* examined by A. Breithaupt, J. Fournet, J. F. Vogl, etc., has a similar formula. F. Beijerinck regards voltzite as an isomorphous mixture of wurtzite and zincite. C. F. Rammelsberg, and J. A. Arfvedson obtained what they regarded as zinc oxysulphide, ZnO.ZnS, by calcining zinc sulphate in a stream of hydrogen. The product was probably a mixture of oxide and sulphide. From J. Percy's experiments **copper oxide** and zinc sulphide appear to decompose each other, forming a button of metal and a regulus. P. Berthier found that with **lead oxide,** sulphur dioxide, lead, and zinc oxide are produced. P. Berthier found that at a white heat, **manganese dioxide** and zinc sulphide furnish sulphur dioxide, zinc oxide, and manganous oxide. V. Lindt, and V. Lepiarczyk found **ferric oxide** reacts quantitatively with zinc sulphide at 1300° in the absence of air, probably $2Fe_2O_3+4ZnS=4FeO+Zn+3ZnS+SO_2=3FeS+Fe+4ZnO+SO_2$; and if carbon is also present, $Fe_2O_3+2ZnS+4C=2Fe+2Zn+3CO+CS_2$. It is possible that the ferric oxide is first reduced by carbon to ferrous oxide and iron, which then react with the zinc sulphide.

J. Lemberg[24] found that an acid soln. of **silver sulphate** reacts with zinc sulphide, forming silver sulphide ; F. Raschig observed that a boiling soln. of **cupric chloride** converts zinc blende into zinc chloride, and cupric sulphide ; and zinc blende with a soln. of **cuprous chloride** in sodium chloride is incompletely converted into zinc chloride and cuprous sulphide. E. Schürmann found precipitated zinc sulphide, at 100°, reacts completely with soln. of cupric sulphate, **cadmium sulphate, stannous chloride,** and **lead nitrate,** but not with soln. of **ferrous sulphate** or **thallium nitrate ;** he also found that cadmium sulphide is completely decomposed by a soln. of cupric sulphate, partially with stannous chloride, and not with **lead acetate, zinc sulphate, nickel sulphate,** or **tartar emetic.** Hot soln. of **ferric chloride** were found by H. Brandhorst to be reduced by zinc sulphide ; G. de Bechi and R. W. Rücker found that zinc sulphide is soluble in **ferric sulphate** soln. and the latter are reduced ; and J. Perino found that with **ferric nitrate** at 150° to 200°, zinc sulphide is oxidized before ferrous sulphide. According to E. A. Parnell, when an intimate mixture of **zinc sulphate** and sulphide is heated, zinc oxide and sulphur dioxide are formed : $ZnS+3ZnSO_4=4ZnO+4SO_2$.

R. Meldrum[25] prepared **colloidal cadmium sulphide** by the action of hydrogen sulphide on a dil. soln.—containing say 0·015 per cent. of cadmium sulphide ; W. Biltz also made colloidal zinc and cadmium sulphides. **Colloidal zinc sulphide** can be prepared in a similar way. As shown by P. Donnini, and J. Hausmann, the ordinary amorphous precipitate forms a colloidal soln. as the adsorbed salts are removed by washing. C. Winssinger obtained colloidal zinc sulphide by passing hydrogen sulphide into water with zinc hydroxide, or ordinary precipitated zinc sulphide in suspension. J. Thomsen obtained the pale opalescent soln. by the action of an alkali hydrosulphide on a dil. soln. of zinc sulphate. V. von Zotta, and L. W. McCay used a similar process. L. Vanino and F. Hartl prepared a gold-yellow clear colloidal cadmium sulphide by treating with hydrogen sulphide a soln. of 0·2 grm. of cadmium sulphate in a litre of water. E. Prost precipitated cadmium sulphide by treating an ammoniacal soln. of cadmium sulphate with hydrogen sulphide, and, suspending the well-washed precipitate in water, treated it anew with hydrogen sulphide. According to J. Hausmann, if a soln. of sodium sulphide in 5 per cent. gelatine, agar-agar, or starch be brought in contact with a dil. aq. soln. of cadmium salt, so that the one soln. can diffuse with the other, a golden-yellow layer of the colloid is formed. Colourless or yellow ammonium sulphide does not work.

A. Müller obtained colloidal zinc sulphide by allowing a mixture of zinc sulphate and glycerol to stand in contact with ammonium sulphide for three days.

Freshly precipitated zinc or cadmium sulphide is often colloidal and contains adsorbed water ; and it then dissolves in acids more readily than the dried sulphide. H. Reinsch found the coagulum retains some chloride when precipitated from soln. of zinc chloride. A sample of precipitated zinc sulphide dried at 100° was found by P. L. Geiger and K. L. Reimann, and H. W. F. Wackenroder to have the composition $2ZnS+H_2O$; H. W. F. Wackenroder, R. Wagner, and A. Souchay found samples dried at 100° had the composition $3ZnS+H_2O$; P. L. Geiger and K. L. Reimann, and A. Souchay, the composition $4ZnS+H_2O$; and by the action of hydrogen sulphide in air-dried zinc hydroxide, $ZnS+nH_2O$. R. Schindler obtained crystalline plates of a hydrate by the action of a very slow current of hydrogen sulphide on a soln. of zinc sulphate. When dried at 37·5°, the composition was $ZnS+H_2O$. S. E. Linder and H. Picton found the composition of the air-dried precipitate corresponded with $3ZnS.2H_2O$. For the heat of hydration of zinc sulphide, *vide supra*. According to W. Biltz, when 1 c.c. of a colloidal soln. of cadmium sulphide is treated with two or three drops of a colloidal soln. of **ferric hydroxide,** yellowish-brown floccules are formed ; colloidal **aluminium hydroxide, chromic hydroxide,** or **zirconium hydroxide** gives a precipitate ; and colloidal **cerium hydroxide** gelatinizes the soln. Plant and animal fibres are coloured yellow by a colloidal soln. of cadmium sulphide. L. Vanino and F. Hartl found that when 100 c.c. of a colloidal soln. of cadmium sulphide with 0·02 grm. of cadmium sulphate are treated with 3 grms. of barium sulphate, a colourless filtrate is obtained.

There are doubts about the individuality of **zinc hydrosulphide,** $Zn(SH)_2$, or **cadmium hydrosulphide,** $Cd(SH)_2$. J. Thomsen added 2 eq. of sodium hydrosulphide to one of zinc sulphate in aq. soln., and obtained an opalescent liquid which when treated with acids or sodium hydroxide gave a precipitate which he regarded as *wahrscheinlicher* zinc hydrosulphide. When the soln. is allowed to stand some hours, a precipitate is formed which redissolves when heated ; he said it is probable that sodium sulphide and hydrosulphide behave similarly towards a soln. of zinc sulphate, and that zinc hydrosulphide dissolves in a soln. of sodium hydrosulphide like zinc hydroxide does in a soln. of sodium hydroxide. V. von Zotta stated that J. Thomsen's hydrosulphide has the formula $Zn(SH)_2.2ZnS$, or $Zn_3H_2S_4$. The production of this substance explains the evolution of hydrogen sulphide when an alkali hydrosulphide is added to zinc sulphate. H. Baubigny prepared the hydrosulphide from soln. of the acetate either by the action of hydrogen sulphide or ammonium sulphide. According to M. Berthelot, the precipitation is incomplete with the chloride or sulphate. The supposed zinc and cadmium hydrosulphides have been studied by S. E. Linder and H. Picton. J. M. van Bemmelen said that the supposed zinc or cadmium hydrosulphide is not a true chemical compound. According to L. W. McCay, zinc sulphide or zinc hydrosulphide precipitated from alkaline soln. of zinc salts by alkali hydrosulphide is soluble in an excess of the reagent much as zinc oxide or hydroxide dissolves in alkali hydroxide. The analogy leads to the assumption that an alkali sulphozincate, R_2ZnS_2, is formed : $Zn(SH)_2+2RSH=R_2ZnS_2+2H_2S$. The **alkali sulphozincate,** however, must be very unstable, for when conc. mineral salts are added, zinc sulphide or hydrosulphide gradually separates out in a slimy form. Zinc hydrosulphide precipitated from alkaline soln. by hydrogen sulphide, dissolves when the current of gas is continued for some time.

H. Schiff [26] treated a neutral soln. of a zinc salt with potassium pentasulphide and obtained a white mass, which, when washed, pressed, and dried over sulphuric acid, furnished a straw-yellow anhydrous mass. The analyses agreed with **zinc pentasulphide,** ZnS_5. When heated in the absence of air, it decomposes into the monosulphide and sulphur ; it also dissolves in acids with the evolution of hydrogen sulphide and the separation of sulphur. He also prepared orange-yellow **cadmium**

pentasulphide, CdS_5, in a similar manner. O. Follenius believes that these products are mixtures of the monosulphides and free sulphur.

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§ 16. Zinc and Cadmium Sulphates

G. W. Schwartze [1] has stated that zinc sulphate, or artificial white vitriol was known near the end of the thirteenth or the beginning of the fourteenth century,

but, according to J. Beckmann, it was not known before the middle of the sixteenth century, and it was first made at Rammelsberg or at Goslar. He said that the white vitriol which is produced in the mines at Rammelsberg in the form of icicles gave rise to the discovery and manufacture of the salt. The native white vitriol was packed in casks and called *Gogkelgut*. The salt was known as *Gallitzenstein*, *Golitzstein*, and *Calitzenstein*. These terms were also applied to green vitriol—possibly derived from galls, because vitriol and galls were used in making inks and in dyeing. The colour of the early preparations mentioned by H. Boerhaave were green, owing to the presence of impurities. G. Agricola called it *charcanthum candidum* or *atramentum sutorium*; C. Gesner called it *atramentum album*, and it was later called *Erzalum*, *vitriolum album*, *white vitriol*, *white copperas*, *zinc vitriol*, etc. N. Lemery (1735), L. Lemery (1707), and E. F. Geoffroy knew that sulphuric acid is one of its constituents, but they were not clear about the basic component. J. F. Henckel found that white vitriol contains zinc, and G. Brandt showed that it consists of sulphuric acid and zinc oxide. J. Hellot confirmed this conclusion.

According to A. Breithaupt,[2] microscopic crystals of zinc sulphate occur as the mineral *zincosite* in Sierra Almagrera (Spain); it was said to be isomorphous with lead and barium sulphates. H. Brandhorst found crystals of zinc sulphate in the flue dust of furnaces roasting zinc sulphide ores. There are doubts about A. Breithaupt's mineral, but heptahydrated zinc sulphate, $ZnSO_4.7H_2O$, occurs as the mineral *goslarite*, in the passages of mines—Goslar (Harz), Schemnitz (Hungary), Fahlun (Sweden), Holywell (Wales), etc.—and is formed by the decomposition of zinc blende. It was described by J. G. Wallerius; and analyzed by F. S. Beudant, and M. H. Klaproth. F. S. Beudant called the mineral *gallitzenite*, but W. Haidinger's term *goslarite* is generally employed. A form of goslarite in which zinc is partially replaced by ferrous iron is called *ferrogoslarite*. It is found in the drainage of some mines. L. Palmeri found crystals of the heptahydrated zinc sulphate among the sublimation products from Vesuvius.

In addition to anhydrous **zinc sulphate,** $ZnSO_4$, hydrates have been reported containing 1, 2, $3\frac{1}{2}$, 5, 6, and 7 mols of water per mol of sulphate; and besides anhydrous **cadmium sulphate,** $CdSO_4$, hydrates with $\frac{1}{2}$, 1, $1\frac{1}{3}$, $2\frac{1}{2}$, $2\frac{2}{3}$, 3, 4, 7, and 9 mols of water per mol of sulphate have been reported. Not all these hydrates can be regarded as chemical individuals. H. G. Denham circulated a soln. of cadmium sulphate over granulated cadmium for several days, and, after 40 hrs., fern-like crystals of cadmium were observed to separate at the bottom of the column of cadmium. It was therefore inferred that the bivalent cadmium is reduced to univalent cadmium: $Cd+CdSO_4=Cd_2SO_4$, and that the **cadmium subsulphate,** Cd_2SO_4, in soln. immediately decomposes into ordinary cadmium sulphate and the metal.

Anhydrous zinc sulphate is made by heating the hydrated salt; H. O. Hofman and co-workers[3] said that 263° was the lowest temp. at which the salt can be dehydrated, and that after 2 grms. have been heated 30–40 hrs., 0·24 per cent. of water still remains. F. Krafft stated that the heptahydrate can be completely dehydrated in vacuo at 210°. A. de Schulten showed that crystals of anhydrous zinc or cadmium sulphate can be obtained by the slow evaporation of a soln. of the sulphates in conc. sulphuric acid; and anhydrous cadmium sulphate, by melting cadmium with ammonium or potassium persulphate. P. Klobb made anhydrous zinc sulphate by heating a mixture of ammonium sulphate and the heptahydrate, and A. J. Boult by heating zinc earths, zinc oxide, etc., with ammonium sulphate in closed vessels at 300°–500°; and the International Chemical Co., by melting and roasting zinc sulphide with alkali hydrosulphate.

A soln. of zinc sulphate is obtained by dissolving the metal or the oxide[4] in dil. sulphuric acid. Similar results are obtained with the carbonate and hydroxide. Zinc sulphate is made by roasting zinc blende and evaporating the soln. in dil. acid for crystallization. F. Ellershausen and R. W. Western recommended extracting the roasted ore with a soln. of ammonium sulphate in sulphuric acid. J. Knobloch

recommended purifying the boiling soln. of zinc sulphate by adding sufficient zinc fluoride to precipitate all the calcium and magnesium, but an excess should not be used, or if used should be removed by gypsum. Zinc oxide, mixed with water, is then added, the whole is left for a day, with occasional stirring, then filtered, acidified with a little sulphuric acid, and the filtrate evaporated till it begins to crystallize. If the crystals contain chlorine, it is necessary to recrystallize from water. E. van de Vyvere, F. Stolba, H. Prunier, and C. J. Bender have described methods for the purification of zinc sulphate—*vide* purification of zinc. C. R. Kuzell and J. R. Marston discussed the purification of zinc sulphate from arsenic. The crystallization of the aq. soln. of zinc sulphate at ordinary temp. furnishes the **heptahydrated zinc sulphate,** $ZnSO_4.7H_2O$; and soln. of cadmium sulphate, **octotritahydrated cadmium sulphate,** $CdSO_4.\frac{3}{8}H_2O$. E. A. Partridge prepared highly purified cadmium sulphate by adding a small excess of sulphuric acid to a soln. of purified cadmium nitrate, evaporating to dryness, and heating the mass until the fumes of sulphur dioxide ceased to be evolved. The residue is then extracted with water, the soln. crystallized, and the crystals dried for 6 hrs. at 200°.

According to C. von Hauer,[5] 100 parts of a sat. soln. of zinc sulphate at 18°–20° contain 35·36 parts of the anhydrous salt. Other observations on the solubility of zinc sulphate have been made by C. J. B. Karsten, E. Tobler, A. B. Poggiale, H. G. F. Schröder, H. Schiff, G. J. Mulder, etc. L. C. de Coppet, F. Rüdorff, F. Guthrie, and G. Bruni made observations at low temp. The best representative values for the percentage solubility in water, with the corresponding solid phases are,

Solid phase	−5°	0·1°	9·1°	15°	25°	35°	39°	
$ZnSO_4.7H_2O$	28·21	28·54	32·01	33·81	36·67	39·98	41·21	per cent. $ZnSO_4$

H. L. Callendar and H. T. Barnes give 39·0° for the transition temp. of the hepta- and hexa-hydrates ; and A. Étard gives 70·0° for the transition temp. of the hexa- and mono-hydrates.

	50°	70°	80°	90°	100°	120°	137°	169°	171°
Per cent. $ZnSO_4$	43·45	47·5	46·4	45·5	44·7	41·7	38·0	30·0	29·0
Solid phase	$ZnSO_4.6H_2O$			$ZnSO_4.H_2O$					

L. C. de Coppet gives for the unstable system at −7·15° and −10·1°, respectively 38·10 and 30·70 per cent. $ZnSO_4$ with ice as the solid phase ; and E. Cohen gives for the unstable hexahydrate at −5°, 0·1°, and 25°, respectively 32·01, 33·10, and 38·93 per cent. $ZnSO_4$. The data are plotted in Fig. 48, to show the ranges of stability of the different hydrates. H. L. Callendar and H. T. Barnes represent the percentage solubility, S, between 0° and 39°, by $S=29{\cdot}5+0{\cdot}270\theta+0{\cdot}00068\theta^2$. E. Cohen also calculated formulæ for the solubility over definite ranges of temp. C. R. Schulze noted a maximum in the solubility curve between 10° and 60°, and A. Étard followed the curve for the decreasing solubility of zinc sulphate up to 171°. E. Cohen and L. R. Sinnige give 57·95 per cent. for the solubility of heptahydrated zinc sulphate at 25° to 26° under one atm. press. ; 58·38 per cent. under 500 atm. press. ; and 57·55 at 1000 atm. press.

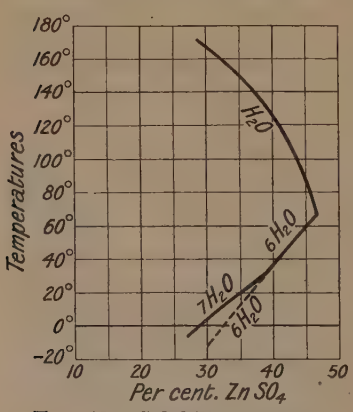

Fig. 48.—Solubility Curve of Zinc Sulphate.

According to R. Schindler,[6] and J. B. Hannay, and T. Graham, **monohydrated zinc sulphate,** $ZnSO_4.H_2O$, is formed when the heptahydrated salt is dried in air at 100°, or in vacuo over sulphuric acid at 20°. F. Krafft also made the monohydrate by 15 hrs.' drying in a vacuum desiccator at a summer's temp. Crystals of the monohydrate also separate when the sulphate is deposited from a boiling sat.

soln.—*vide* Fig. 48—the composition of the crystals, said E. Cohen, remains constant when allowed to stand on the water-bath for a long time. A. Étard made the monohydrate by heating to 200° an excess of conc. sulphuric acid with a sat. soln. of zinc sulphate, and cooling. R. Schindler found that crystals of the heptahydrate at 50° crumble to a white powder, which he regarded as **dihydrated zinc sulphate,** $ZnSO_4.2H_2O$; he also obtained a crystalline crust of crystals with the same composition by evaporating at 100°, a soln. of zinc sulphate with an excess of sulphuric acid. A. Étard also obtained crystals of the dihydrate from a soln. of zinc sulphate at a temp. over 81°. J. B. Hannay, and O. B. Kühn obtained a similar product as a crystalline powder by adding sulphuric acid to a boiling conc. soln. of zinc sulphate. E. F. Anthon, and R. J. Kane obtained rhombohedral crystals of **hemiheptahydrated zinc sulphate,** $ZnSO_4.3\frac{1}{2}H_2O$, mixed with crystals of the heptahydrate, by allowing a conc. aq. soln. of zinc sulphate containing a little free acid, to stand for some time at 0°. J. B. Hannay's study of the heating curves led him to suppose that this salt is **trihydrated zinc sulphate,** $ZnSO_4.3H_2O$. R. Schindler obtained a crust of crystals of what he regarded as **pentahydrated zinc sulphate,** $ZnSO_4.5H_2O$, by evaporating the soln. of zinc sulphate between 40° and 50°. O. B. Kühn also prepared the same compound by boiling the finely powdered heptahydrate with alcohol of sp. gr. 0·856; the pasty mass solidifies to a hard crystalline substance with a waxy fracture. J. B. Hannay obtained the pentahydrate in a similar manner. E. Mitscherlich, and J. B. Hannay found that crystals of **hexahydrated zinc sulphate,** $ZnSO_4.6H_2O$, separate from aq. soln. at a temp. over 30°—J. C. G. de Marignac said 50°–55°. According to E. Mitscherlich, also, a crystal of the heptahydrate when heated over 52° becomes opaque because it is thereby converted into an aggregate of small crystals of the hexahydrate; E. Wiedemann converted the crystals of the heptahydrate into those of the hexahydrate by heating at 69°. E. Cohen gave 38·75° for the transition temp. by vol. measurements, 38·50° by solubility measurements, and 39·0° by conductivity measurements. H. L. Callendar and H. T. Barnes gave 39·95° for the transition temp.; H. T. Barnes, and H. T. Barnes and H. L. Cooke gave 39·95° from solubility determinations, and 38·75° from measurements on the e.m.f. of a Clarke's cell. L. de Boisbaudran observed a change in the character of the crystals of the heptahydrate between 50° and 60°; and R. Hollmann, at about 40°.

The solubility of cadmium sulphate in water has been measured by P. Kohnstamm and E. Cohen,[7] H. von Steinwehr, J. Koppel and A. Gumpertz, H. B. Holsboer, etc. R. Mylius and R. Funk's values for the percentage solubility for the heptahydrate as solid phase, are 44·5, 46·1, and 49·5 per cent. $CdSO_4$ respectively at −17°, −10°, and −6°. The best representative values for the $2\frac{2}{3}$ hydrate and the monohydrate are:

	−18°	0°	20°	40°	74°	77°	85°	100°	112°
$CdSO_4$	43·35	43·01	43·37	43·99	46·70	42·2	39·6	37·8	37·0
Solid phase	$CdSO_4.2\frac{2}{3}H_2O$					$CdSO_4.H_2O$			

The transition point for $CdSO_4.2\frac{2}{3}H_2O$ by F. Mylius and R. Funk is 74°, and for $CdSO_4.H_2O \rightleftharpoons CdSO_4 + H_2O$ is 112°; for the latter, N. Worobieff gave 104°. A. Étard's values at 120°, 160°, and 200° are respectively 31·50, 16·70, and 2·25 per cent. $ZnCO_4$, and the solid phase was not determined. The observed results are shown in Fig. 49, which shows the ranges of stability of the different hydrates. E. Cohen and L. R. Sinnige found for the solubility at 1, 500, and 1000 atm. press. respectively 76·80 (25°), 77·85 (25°), and 78·79 (25·6°) per cent. $CdSO_4$. P. Kohnstamm and E. Cohen reported a change in the solubility curve of cadmium sulphate in water at 15°, but H. von Steinwehr found the curve to be continuous between 13·7° and 25°. E. Cohen and J. J. Wolters found a minimum in the solubility curve of $CdSO_4.2\frac{2}{3}H_2O$ at about −9°. The number of grams of $CdSO_4$ per 100 grms. of sat. soln. in the neighbourhood of this temp. was found to be 43·047 at −3·00°; 43·020 at −6·00°; 43·008 at −9·00°; and 43·029 at −12·00°.

O. B. Kühn[8] prepared crystals of what have been regarded as **hemihydrated cadmium sulphate,** $CdSO_4.\frac{1}{2}H_2O$, by decomposing a third part of a soln. of cadmium sulphate with potassium hydroxide, and boiling the product with the remaining two-thirds of the soln. According to the same authority, crusts of ill-defined crystals of **monohydrated cadmium sulphate,** $CdSO_4.H_2O$, are obtained by evaporating a soln. of cadmium sulphate containing an excess of sulphuric acid; and C. von Hauer obtained the same hydrate by adding conc. sulphuric acid to a boiling soln. of cadmium sulphate. H. Lescœur added an equal vol. of sulphuric acid to a sat. aq. soln. of the sulphate. F. Mylius and R. Funk obtained crystals by evaporating the neutral aq. soln. between 80° and 100°. H. C. Jones and H. P. Bassett, and N. Worobieff crystallized the soln. at 103° to 104°—*vide* Fig. 49. G. Wyrouboff prepared the monohydrate by heating the ordinary sulphate with twice the amount of sulphuric acid at 30°–40°, if more sulphuric acid be used, the crystallization is conducted at a lower temp. N. Worobieff claimed to have made monoclinic crystals of **hemitrihydrated cadmium sulphate,** $CdSO_4.1\frac{1}{2}H_2O$, by crystallization from a soln. of zinc-free cadmium oxide in dil. sulphuric acid. **Octotritahydrated cadmium sulphate,** $CdSO_4.2\frac{2}{3}H_2O$, crystallizes from sat. soln. at ordinary temp. J. W. Retgers suggests that the octotritahydrate is really trihydrated cadmium sulphate, $CdSO_4.3H_2O$, and this is not outside the limits of the experimental errors in the various analyses which have been reported. F. Stromeyer's observations agree with the formula $CdSO_4.4H_2O$; C. F. Rammelsberg's, N. Worobieff's, and H. Kopp's with $CdSO_4.3H_2O$; C. von Hauer's with $CdSO_4.2\frac{2}{3}H_2O$. F. Mylius and R. Funk consider that **tetrahydrated cadmium sulphate,** $CdSO_4.4H_2O$, may possibly exist since cadmium sulphate forms mixed crystals with tetrahydrated manganese sulphate. H. Lescœur also reported the formation of the tetrahydrate. H. Rose obtained crystals of what he regarded as **hemipentahydrated cadmium sulphate,** $CdSO_4.2\frac{1}{2}H_2O$, by crystallization from a hot soln. of the sulphate—F. Mylius and R. Funk doubt the existence of this hydrate. According to F. Mylius and R. Funk, a crystalline powder of **heptahydrated cadmium sulphate,** $CdSO_4.7H_2O$, is obtained by rapidly cooling to 0° a soln. of cadmium sulphate, sat. at 70°, and then lowering the temp. to —20°, and rubbing the sides of the vessel with a glass rod. H. C. Jones and H. P. Bassett claimed to have made **enneahydrated cadmium sulphate,** $CdSO_4.9H_2O$, by crystallization at a very low temp. The product is possibly a mixture of the cryohydrate and ice. *The mono-, hexa-, and hepta-hydrates of zinc and cadmium sulphates, and the octotritahydrate of cadmium sulphate are the only ones whose individuality can be regarded as definitely established.*

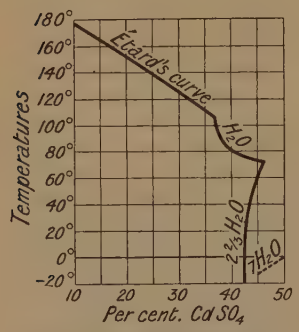

Fig. 49.—Solubility Curve of Cadmium Sulphate.

A. de Schulten[9] prepared **crystals** of anhydrous zinc and cadmium sulphates in rectangular plates; the crystals of the two salts are isomorphous, and belong to the rhombic system. P. Klobb obtained colourless octahedral crystals of zinc sulphate. According to G. Wyrouboff, the crystals of monohydrated cadmium sulphate belong to the monoclinic system, and have axial ratios $a:b:c=1{\cdot}0976:1:1{\cdot}7180$, and $\beta=90°\ 13'$. C. F. Rammelsberg also found the crystals of octotritahydrated cadmium sulphate to belong to the monoclinic system, and have axial ratios $a:b:c=0{\cdot}7992:1:0{\cdot}6900$, and $\beta=117°\ 58'$; C. F. Rammelsberg said the crystals are isomorphous with didymium and yttrium sulphates; H. Kopp, and H. de Sénarmont also have made observations on these crystals. G. Wyrouboff found that the prismatic crystals of hexahydrated zinc sulphate belong to the monoclinic system and have axial ratios $a:b:c=1{\cdot}3847:1:1{\cdot}6758$, and $\beta=98°\ 12'$; J. C. G. de Marignac showed that the crystals are isomorphous with those of the analogous salts of magnesium, nickel, and cobalt. E. Mitscherlich supposed the hexahydrate to be a dimorphous

form of the heptahydrate. L. de Boisbaudran found that when a soln. of zinc sulphate is seeded with the tetragonal form of hexahydrated nickel sulphate, a tetragonal zinc salt is produced. The crystals of goslarite, or heptahydrated zinc sulphate, are bisphenoidal, belong to the rhombic system, and, according to H. J. Brooke, have axial ratios $a : b : c = 0{\cdot}9804 : 1 : 0{\cdot}5631$. C. F. Rammelsberg studied mixed crystals of heptahydrated zinc sulphate with the isomorphous salts of magnesium, manganese, copper, and iron. This subject has also been studied by K. van Hauer, H. Schiff, L. de Boisbaudran, J. Lefort and J. Nicklès, M. Schäuffele, H. Vohl, C. Weltzien, J. Grailich, J. M. Thomson, C. Frenzel, etc. According to J. W. Retgers, the crystals of heptahydrated cadmium sulphate are isomorphous with the corresponding heptahydrated ferrous sulphate. W. Haidinger, and H. Reinsch have reported modifications in the form of heptahydrated zinc sulphate, and E. von Fedoroff obtained an unstable easily soluble monoclinic variety from undercooled soln. According to H. G. F. Schröder, an easily soluble form separates from undercooled soln. protected from air by cotton wool, while if the soln. be crystallized while exposed to the air, or if the crystals be kept in contact with air, a less soluble form is produced.

The **specific gravity** of anhydrous zinc sulphate was given by C. J. B. Karsten,[10] and E. Filhol as 3·400; C. Pape gave 3·436 (16°); P. A. Favre and C. A. Valson, 3·40; H. G. F. Schröder gave 3·551; T. E. Thorpe and J. I. Watts, 3·6235 (15°); and L. Playfair and J. P. Joule, 3·681 (3·9°). H. G. F. Schröder gave 4·447 for anhydrous cadmium sulphate. For monohydrated zinc sulphate, C. Pape gave 3·215 (16°); H. G. F. Schröder, 3·076; L. Playfair, 3·259; and T. E. Thorpe and J. I. Watts, 3·2845 (15°). H. J. Buignet gave 2·939 for monohydrated cadmium sulphate. T. E. Thorpe and J. I. Watts gave 2·958 (15°) for dihydrated zinc sulphate; 2·206 (15°) for the pentahydrate; and 2·072 (15°) for the hexahydrate. For the last-named salt, L. Playfair gave 2·056. For octotritahydrated cadmium sulphate, C. H. D. Bödeker gave 3·05 (12°). The number for heptahydrated zinc sulphate reported by J. H. Hassenfratz is 1·912; by L. Playfair and J. P. Joule, 1·931; by E. Filhol, 2·036; by H. Schiff, 1·953; by H. J. Buignet, 1·957; by P. A. Favre and C. A. Valson, 1·981; by F. Stolba, 1·9534; by S. Holker, 1·976 (15·5°); by C. Pape, 1·901 (16°); by H. G. F. Schröder, 1·984; by H. Töpsöe and C. Christiansen, 2·008; by W. C. Smith, 1·961; and by T. E. Thorpe and J. I. Watts, 1·974 (15°).

The sp. gr. of soln. of zinc sulphate measured at 15° by G. T. Gerlach,[11] when the conc. of the soln. is expressed by the percentage amount of $ZnSO_4.7H_2O$, are:

Conc.	5	10	15	20	25	30	40	50	60
Sp. gr.	1·0288	1·0593	1·0905	1·1236	1·1574	1·1933	1·2709	1·3532	1·4451

Other measurements have been made by H. Schiff, H. L. Callendar and H. T. Barnes, F. Kohlrausch and W. Hallwachs, J. Wagner, J. A. Ewing and J. G. McGregor, C. Charpy, H. C. Jones and F. H. Getman, P. A. Favre and C. A. Valson, W. W. J. Nicol, H. Schiff, C. R. A. Wright and C. Thompson, J. I. Watts, C. Bender, etc. The variation in the sp. gr. of soln. with temp. was measured by O. Grotrian, F. Fouqué, C. Forch, and J. de Lannoy, and their data show the coeff. of thermal expansion of soln. of zinc sulphate—*vide infra*. I. Traube gave for the mol. vol.

Per cent. $ZnSO_4$	2·80	5·61	11·22	16·83	28·08	33·66	100
Mol. vol.	0·5	0·5	3·4	6·3	11·4	13·9	46·3

Per cent. $ZnSO_4.7H_2O$	5	10	20	30	40	60	100
Mol. vol.	126·6	126·7	129·5	132·4	134·3	140·0	142·8

W. Hallwachs, and W. W. J. Nicol also made observations on the mol. vol. of soln. of zinc sulphate. According to R. Broom, when a soln. of 48·36 parts of zinc sulphate in 100 of water is mixed with an equal vol. of water, a contraction of 0·835 per cent. occurs. F. Kohlrausch and W. Hallwachs reported a marked condensation in crystallizing from water. O. Grotrian found for the sp. gr. of soln. of cadmium sulphate at 18°, when the conc. is expressed in per cent. of $CdSO_4$:

Conc.	0·282	1·011	5·08	10·11	25·03	36·07
Sp. gr.	1·0085	1·0085	1·0495	1·1039	1·2955	1·4756

Other determinations have been made by C. A. Valson, J. Kanonnikoff, I. Traube, H. Jahn, O. Schönrock, M. le Blanc and P. Rohland, E. Cohen and L. R. Sinnige, F. Fouqué, F. J. Wershoven, J. Wagner, J. G. McGregor, H. C. Jones and F. H. Getman, R. de Muynck, C. M. Pasea, C. R. A. Wright and C. Thompson, etc. According to E. Irueste, for a soln. of cadmium sulphate of sp. gr. D, at 15°, when that of water at 15° is D_0, the soln. will contain $0{\cdot}91660(D-D_0)-0{\cdot}22101(D-D_0)^2$ grms. of salt per gram of soln. O. Grotrian measured the **fluidity** of soln. of zinc sulphate; G. Quincke,[12] the **specific cohesion ;** and C. A. Valson, W. Grabowsky, E. Klupathy, P. Volkmann, and I. Traube the **rise in capillary tubes** of different diameter. The viscosities of equimol. soln. of magnesium and zinc sulphates were found by J. Wagner to be nearly the same, and he gave, at 25°, for the **viscosity** of zinc and cadmium sulphates, water unity,

	N-	$\frac{1}{2}N$-	$\frac{1}{4}N$-	$\frac{1}{8}N$-
Viscosity $ZnSO_4$	1·3671	1·1726	1·0824	1·0358
Viscosity $CdSO_4$	1·3476	1·1574	1·0780	1·0335

Other measurements were made by S. Arrhenius, L. Grossmann and A. A. Blanchard. The **capillary constant,** of zinc sulphate soln., sp. gr. 1·153, at 20°, was found by E. Klupathy to be 11·9 ; and G. Quincke, I. Traube, and P. Volkmann made similar observations. C. Forsch, A. Brümmer, H. Sentis, P. Volkmann, and I. Traube made observations on the **surface tension** of soln. of zinc sulphate ; and N. E. Dorsey found for soln. of normality N, in dynes per cm. :

N	0	0·066	0·108	0·286	0·372	0·414
σ	73·39	73·30	73·44	73·90	73·79	73·91

I. Traube measured the surface tension of soln. of zinc sulphate in ethyl alcohol. The coeff. of **diffusion** was found by J. J. Coleman to be smaller with soln. of zinc sulphate than with soln. of magnesium sulphate. J. C. Graham, J. H. Long, N. van de Wall, J. Schuhmeister, H. F. Weber, B. von Tietzen-Hennig, and C. Lüdeking have measured the velocity of diffusion of soln. of zinc sulphate. W. Seitz found $k=0{\cdot}2355$ for soln. with 1·0 mol of $ZnSO_4$ per litre at 14·77° ; and G. Thovert found $k=0{\cdot}50$, 0·47, 0·36, and 0·33 respectively at 19·5° for soln. with 0·025, 0·050, 0·55, and 2·95 mol per litre. W. Seitz and J. J. Coleman of soln. of cadmium sulphate ; the former found $k=0{\cdot}246$ at 19° for soln. with two mols of $CdSO_4$ per litre. O. Schmidt found for the **compressibility,** β, of aq. soln. of zinc sulphate between 16° and 17·5° :

Per cent. $ZnSO_4$	7·5	13·5	17·5	32·5	41·0
$\beta\times10^6$	45·1	41·0	41·6	32·3	26·4

W. Watson also measured this constant. When crystals of zinc heptahydrate were warmed from 18° to 40°, G. Wiedemann found a regular increase in vol., at 40° there is a marked change attended by the loss of a mol of water ; between 40° and 69°, there is again a regular expansion ; and at 69° there is an abrupt contraction. There is a marked expansion between 69° and 100°, and a white powder is formed. The relative vol. of aq. soln. of zinc sulphate at different temp. $\delta v=(v-1)10^5$; or $v=(v_0+\delta v)10^{-5}$ when $v_0=100{,}000$, as measured by C. Forch, is :

	5°	10°	15°	20°	30°	40°
0·500N-	27	84	168	278	564	930
1·000N-	55	135	239	364	672	1050
1·999N-	99	213	344	491	830	1227

and his values for the **coefficient of thermal expansion** between 0° and 15° for $\frac{1}{2}N$-, N-, and $2N$-soln. of zinc sulphate, are 0·000054, 0·000110, and 0·000195 respectively. R. Meyer measured the thermal expansion of conc. soln. of zinc sulphate. J. de Lannoy[13] obtained for $v\times10^{-5}$:

Per cent. $ZnSO_4.7H_2O$	20°	40°	60°	80°
4	215	860	1800	3020
10	326	976	1902	3103
20	438	1148	2100	3290
30	550	1291	2251	3390

W. W. J. Nicol found the apparent vol. of supersaturated soln. of zinc sulphate to change quite regularly between 20° and 30°. G. Jäger[14] represented the **thermal conductivity** of 16 and 32 per cent. soln. of zinc sulphate by 95·3 and 91·5 respectively when that of water is 100. H. F. Weber gave for the absolute conductivity, k, at 4·5° :

Sp. gr.	1·134	1·272	1·362	1·362	1·362
k	0·00118	0·00116	0·00115	0·00129 (23·4°)	0·00144 (45·2°)

C. G. Lundquist, and L. Grätz, also made measurements of this constant.

C. Pape[15] gave 0·328 for the **specific heat** of heptahydrated zinc sulphate between 17° and 23° ; H. Kopp gave 0·347 between 15° and 30° ; H. Schottky, 0·3485 between 1° and 34° ; E. Cohen and co-workers, 0·3184 between 18·5° and 22·5° ; and F. Pollitzer gave for the mol. ht. of $ZnSO_4.7H_2O$.

	−191°	−190°	−187°	−185°	−72°	−69°	−65°
Mol. ht.	30·34	31·65	31·76	31·26	67·0	66·9	67·9

J. C. G. de Marignac found the sp. ht. of a soln. of a mol of zinc sulphate with 50, 100, and 200 mols H_2O to be respectively 0·8420, 0·9106, and 0·9523 between 20° and 52°. E. Cohen and co-workers found the sp. ht. of octotritahydrated cadmium sulphate to be 0·2008 at 20°, and the mol. ht. 5·50. Measurements were made by H. Teudt, E. Cohen and A. L. T. Mösveld, J. Thomsen, S. Pagliani, H. Suominen, and H. F. Weber. The sp. ht. of soln. of one mol of cadmium sulphate with n mols of water was found to be

n	500	200	100	50	25	17	14·9	14·4
Sp. ht.	0·972	0·940	0·893	0·813	0·696	0·638	0·615	0·610

According to H. St. C. Deville and H. Debray,[16] the **action of heat** on anhydrous zinc sulphate results in the formation of a basic sulphate, and at an incipient white heat, zinc oxide is formed. J. L. Gay Lussac made some observations on this subject. G. H. Bailey said that zinc sulphate begins to decompose at 427°. H. O. Hofman and co-workers said that the temp. of incomplete decomposition is 528°, and of complete decomposition 739°, and there is no sign of a break in the decomposition curve such as might occur if a true basic salt were formed, and F. O. Doeltz and C. A. Graumann believe the alleged basic sulphate is a mixture of zinc oxide and sulphate ; they add that the reaction $ZnSO_4=ZnO+SO_3$ is reversible. L. and P. Wöhler and W. Plüddemann measured the decomposition press. of anhydrous zinc sulphate—*vide* the action of oxygen on zinc sulphide. H. Pommerenke found the decomposition of zinc sulphate occurs at a lower temp. if it be mixed with zinc oxide. W. A. Tilden gave 50° for the **melting point** of heptahydrated zinc sulphate ; G. Wiedemann, 70·5° ; G. Calcagni and D. Marotta, and O. Ruff and W. Plato gave 1000° for the m.p. of anhydrous cadmium sulphate, and the latter say that there is a marked thermal effect at 820°, indicating that some transformation is taking place ; mixtures of cadmium sulphate and chloride gave a V-eutectic at about 569° and 85 molar per cent. of the chloride. E. Cohen found −3752 cals. for the **heat of fusion** of heptahydrated zinc sulphate ; and he calculated −3609 cals. from J. Thomsen's data.

T. Graham, O. B. Kühn, and A. van der Toorn found that crystals of heptahydrated zinc sulphate effloresce in air, and at 100°, they lose $6H_2O$, and the remaining water is expelled at a red heat ; T. Graham applied the term *saline water* to this portion of the water of crystallization which is not expelled except at a relatively high temp., and J. I. Pierre stated that all the water can be slowly expelled from the heptahydrate in a current of dry air at 110°. A. Frenzel drove off 39·75 of the

contained 43·90 per cent. of water by heating goslarite to 100°. H. Baubigny showed that the speed of efflorescence in air is directly proportional to the vap. press. The neutral salt effloresces until one of the lower hydrates is formed ; but if acid, all the water can be removed in dry air. F. Krafft removed six mols of water in 15 hrs. at a summer's heat in vacuo, and all was expelled in vacuo at 210°. J. B. Hannay measured the speed of dehydration at 100°, and inferred that at lower temp. hepta-hydrated zinc sulphate is less stable than the corresponding magnesium sulphate. C. R. Schulze, W. Müller-Erzbach, P. C. F. Frowein, and C. E. Linebarger have measured the **vapour pressure,** p, of hydrated zinc sulphate, and G. Wiedemann found in mm. of mercury :

	16·5°	30°	40°	50°	60°	70°	78·8°	88°
p . .	7·3	20·2	44·2	73·1	113·9	170·8	258·5	116·6

and P. C. F. Frowein gave for the maximum press. in mm. of mercury :

	$ZnSO_4.7H_2O$				$ZnSO_4.6H_2O$			
	18·00°	20·45°	25·15°	29·95°	17·85°	25·15°	29·95°	31·70°
p . .	8·046	10·075	14·697	2·389	7·633	13·286	18·826	21·075

H. Lescœur found the vap. press. curves furnished evidence of the existence of mono- and hepta-hydrated zinc sulphates.

A. van der Toorn showed that monohydrated zinc sulphate does not lose its water until the temp. exceeds 100° ; T. Graham said the water is not lost even at 205°, but is given off near 238° ; and T. Thomson, R. Schindler, and H. G. F. Schröder, found a little sulphuric acid is also lost at this temp. For the transformation of the hepta- into the hexa-hydrate see the preparation of the latter. According to F. Mylius and R. Funk, when the temp. of heptahydrated cadmium sulphate rises to 4°, it slowly decomposes, forming a mush which contains the octotritahydrate. The vap. press. of the last-named salt was measured by A. H. Pareau, by H. Precht and K. Kraut, and H. Lescœur. C. D. Carpenter and E. R. Jette found the transition temp. between the octo- and tri-hydrates to be 41·5°, and they also measured the vap. press. of the solid and sat. soln. Unlike C. von Hauer, F. Mylius and R. Funk found that crystals of monohydrated cadmium sulphate can be heated to 100° without change, but at 160°, the greater part of the combined water is expelled ; they also obtained no signs of the intermediate formation of the hemihydrate of O. B. Kühn during the dihydration of the monohydrate. According to H. Lescœur, the dissociation press. of the monohydrate is 162 mm. at 174·5°, and immeasurably small at 0°. To summarize for the 6–7 hydrates at 25°, H. W. Foote and S. R. Scholes gave 13·6 mm. ; P. C. F. Frowein, 14·6 mm. ; W. C. Schumb, 15·34 mm. ; H. Lescœur, 14·0 ; W. Müller-Erzbach, 12·9 mm. ; and G. Wiedemann, 14·5 mm. For the 1–6 hydrates, H. W. Foote and S. R. Scholes gave 12·8 mm. ; P. C. F. Frowein, 13·2 mm. ; W. Müller-Erzbach, 11·7 mm. ; and A. A. Noyes and L. R. Westbrook, 13·0 mm. For the 0–1 hydrates, H. W. Foote and S. R. Scholes gave 1·0 mm., and W. Müller-Erzbach, 0·5 mm. E. Cohen and co-workers measured the effect of press. on the transition temp. of heptahydrated zinc sulphate.

G. Tammann [17] measured the vap. press. of aq. soln. of zinc sulphate at 100°, and found that with soln. containing 15·59, 35·76, and 77·72 grms. of $ZnSO_4$ per 100 grms. of water, the vap. press. of water was lowered 10·0, 25·4, and 87·0 mm. ; similarly with aq. soln. containing 16·46, 31·21, and 49·92 grms. of $CdSO_4$ per 100 grms. of water, the vap. press. of water was lowered 7·1, 12·9, and 23·3 mm. respectively. G. Tammann also measured the vap. press. of soln. of zinc sulphate in water at different temp. The lowering of the vap. press. has been measured by R. Emden, and J. Moser. J. Walker found the percentage mol. lowering of soln. with a mol of $ZnSO_4$ in 100 mols of water to be 1·26. For soln. of zinc sulphate containing n mol of $ZnSO_4$ in 1000 mols of water, H. Hausrath found for soln. with up to n=0·03191, and H. C. Jones and F. H. Getman for soln. with up to n=2·032 for the **lowering of the freezing point,** δf:

n	0·0002363	0·006259	0·01391	0·051	0·102	1·015	0·032
δf	0·000808°	0·01786°	0·03701°	0·094°	0·194°	1·753°	4·990°
$\delta f/n$	3·467	2·886	2·661	1·84	1·90	1·72	2·46

Values for aq. soln. of zinc sulphate have also been obtained by F. Rüdorff, N. Tarugi and G. Bombardini, F. M. Raoult, L. Kahlenberg, S. Arrhenius, L. C. de Coppet, G. Tammann, etc. For cadmium sulphate soln. with n mol of $CdSO_4$ per 1000 grms. of water, H. Hausrath found for soln. with up to n=0·03120, and H. C. Jones and F. H. Getman for soln. with up to n=1·250:

n	0·0002388	0·002685	0·03120	0·063	0·500	1·000	1·250
δf	0·0008417°	0·008189°	0·07556°	0·201°	1·259°	2·870°	4·160°
$\delta f/n$	3·526	3·055	2·421	3·19	2·52	2·87	3·23

Data were also obtained by F. M. Raoult, N. Tarugi and G. Bombardini, H. C. Jones and B. P. Caldwell, L. Kahlenberg, S. Arrhenius, D. J. Davis and R. E. Fowler, etc. F. Guthrie found the **cryohydric or eutectic temperature** of zinc sulphate to be −5°; L. C. de Coppet gave −6·55° for soln. with 37·3 parts of $ZnSO_4$ in 100 parts of water; J. Koppel and A. Gumpertz found −6·5°; G. Bruni, −6·4°; for cadmium sulphate, J. Koppel and A. Gumpertz gave −16·8°; and F. Mylius and R. Funk, −17°.

According to T. Griffiths, the **boiling point** of a sat. soln. of zinc sulphate—85 grms. of salt in 100 grms. of water—is 104·4°; and G. T. Gerlach gave for soln. with w grms. of $ZnSO_4$ in 100 grms. of water:

w	13·1	25·0	37·7	45·4	53·9	61·0	74·9	85·7
B.p.	100·5°	101°	101·5°	102°	102·5°	103°	104°	105°

L. Kahlenberg found for the raising of the b.p. of water at 742–3 mm. press.:

w $ZnSO_4$	2·886	10·139	22·202	30·47	35·18	39·83	41·30	44·56
Rise of b.p.	0·080°	0·266°	0·591°	0·899°	1·122°	1·381°	1·459°	1·671°
w $CdSO_4$	4·563	10·972	20·662	27·777	36·76	41·28	47·38	53·47
Rise of b.p.	0·105°	0·215°	0·356°	0·494°	0·699°	0·820°	0·988°	1 164°

Other measurements with cadmium and zinc sulphates were made by N. Tarugi and G. Bombardini.

According to M. Berthelot,[18] the **heat of formation** of anhydrous zinc sulphate is (Zn, S, 40), 229·6 to 233·4 Cals.; R. de Forcrand gave 230·91 Cals. and J. Thomsen gave for (Zn, O_2, SO_2), 158·99 Cals. J. Thomsen also gave for (Cd, S, 4O), 222·55 Cals., and M. Berthelot, 219·9 Cals. W. Nernst calculated the free energy of formation of hexa- and mono-hydrated zinc sulphates. L. and P. Wöhler and W. Plüddemann give 36 Cals. for the heat of decomposition $ZnSO_4=ZnO+SO_3$. From his observations on the **heat of hydration** of zinc sulphate, J. Thomsen inferred that zinc sulphate forms hydrates with 1, 3, 4, 6, and 7 mols of water; and he gave 8·08 Cals. for the heat of hydration of $CdSO_4.2\frac{2}{3}H_2O$. E. Cohen and co-workers gave 7·890 Cals. for the heat of hydration of $CdSO_4$ to form $CdSO_4.2\frac{2}{3}H_2O$. For (Zn, O_2, SO_2, H_2O) J. Thomsen gave 167·47 Cals., and for the heat of soln., Q Cals. of $ZnSO_4.nH_2O$ in 400 mols of water at 18°; and hence for the heat of hydration, Q_1 Cals., $ZnSO_4+nH_2O$:

n	0	1	2	3	4	5	6	7
Q	10·434	9·950	7·604	5·258	3·513	1·335	−0·843	−4·260
Q_1	—	8·484	10·830	13·176	14·921	17·099	19·277	22·694

P. C. F. Frowein calculated 2·280 Cals. for the heat of soln. of the hexahydrate, and −3·44 Cals. for that of the heptahydrate. For the **heat of neutralization,** $H_2SO_{4soln.}+ZnO=ZnSO_{4soln.}+H_2O+23·4$ Cals., J. C. G. de Marignac gave 22·3 Cals. J. Thomsen gave for the **heat of solution** of a mol of $ZnSO_4$ in 400 mols of water at 18°, 18·4 Cals.; and for $ZnSO_4.7H_2O$, −4·3 Cals.; P. A. Favre and C. A. Valson found for the heat of soln. of $ZnSO_4.nH_2O$:

n	0	1	3·75	4·46	4·55	6·17
Heat of soln.	9·289	4·812	2·205	1·354	1·198	−0·397 Cals.

and 5·455 Cals. for the heat of soln. of an eq. of cadmium sulphate in a litre of water. J. Thomsen gave 10·74 Cals. for the heat of soln. of a mol of cadmium sulphate in 400 mols of water, and 6·05 Cals. for the monohydrate. E. Cohen, W. D. Heldermann, and A. L. T. Mösveld, made observations on the heat of soln. of cadmium sulphate in soln. of the same salt. For the heat of soln. of $CdSO_4.H_2O$, P. A. Favre and C. A. Valson gave 6·2 Cals.; for $CdSO_4.2\frac{2}{3}H_2O$, 2·7 Cals.; and for $CdSO_4.3H_2O$, 3·062 Cals. J. Thomsen gave for the **heat of dilution** of a soln. of a mol of $ZnSO_4$ in 20 mols of water with 50, 100, and 200 mols of water respectively, 318, 369, and 385 Cals. Observations were also made by C. R. A. Wright and C. Thompson, J. H. Pollock, and L. C. de Coppet; for the heat of dilution of a soln. with $n CdSO_4.100H_2O$ down to $0·25CdSO_4.100H_2O$, C. R. A. Wright and C. Thompson gave:

n	1	2	3	4	5	6	7
Heat of dilution	75	275	450	635	825	1075	1450

According to A. des Cloizeaux,[19] the crystals of hexa- and hepta-hydrated zinc sulphates and of octotritahydrated cadmium sulphate have a negative **double refraction.** H. Töpsöe and C. Christiansen found the **index of refraction** of hepta-hydrated zinc sulphate to be for the C-line, $\alpha=1·4544$, $\beta=1·4776$, and $\gamma=1·4812$; for the F-line, $\alpha=1·4568$, $\beta=1·4801$, and $\gamma=1·4836$; and for the D-line, $\alpha=1·45683$, $\beta=1·4801$, and $\gamma=1·48445$. H. C. Jones and F. H. Getman found the refractive index, μ, for soln. with C mols of zinc sulphate per litre:

C	0·051	0·102	0·203	0·406	0·609	1·015	1·624	2·032
μ	1·32711	1·32814	1·33110	1·33618	1·34149	1·35151	1·36543	1·37455

and for soln. with C mols of cadmium sulphate per litre:

C	0·063	0·125	0·250	0·500	0·625	0·875	1·000	1·250
μ	1·32790	1·33037	1·33535	1·34466	1·34912	1·35799	1·36101	1·37028

J. Kanonnikoff, C. Chéneveau, W. Hallwachs, H. Dijken, C. A. Valson, F. Fouqué, P. Barbier and L. Roux, M. le Blanc and P. Rohland, H. Jahn, R. de Muynck, etc., determined the optical constants for soln. of zinc and cadmium sulphates. O. Schönrock found the specific and **molecular rotation of the plane of polarization** for soln. of cadmium sulphate of sp. gr. 1·36289 (16°/4°) to be respectively 0·3423 and 3·955; and for soln. of sp. gr. 1·2421 (16°/4°), respectively 0·3597 and 4·156; H. Jahn gave for soln. of sp. gr. 1·1781 (20°/20°), the respective values 0·44748 and 5·17. J. R. Collins measured the **ultra-red absorption spectrum** of aq. soln. of the sulphate.

According to E. Wiedemann and G. C. Schmidt,[20] dried heptahydrated zinc sulphate gives a pale yellow **cathodo-luminescence,** with a prolonged after-glow which is white when the salt is heated; if one per cent. of manganese sulphate is present, the luminescence is an intense red, and the spectrum shows a red band. The property of showing **thermoluminescence** is lost in about a week. The photo-luminescence is red. J. A. Wilkinson found purified cadmium sulphate does not give cathodo-luminescence; the less pure salt has a yellow fluorescence, and H. Longchambron studied the spectrum of the **triboluminescence** of cadmium sulphate. E. Wiedemann and G. C. Schmidt found the spectrum of anhydrous cadmium sulphate shows intense lines in the yellowish-green, and feeble ones in the red and blue. A solid soln. of cadmium sulphate with one per cent. of zinc sulphate gives a blue thermoluminescence. G. C. Schmidt found the **canal rays** incite a yellow luminescence with calcined cadmium sulphate, but the property is lost with prolonged action. H. Greinacher found that **radioactive rays** raise the temp. of cadmium sulphate less than 0·01°. E. Goldstein studied the cathodo-luminescence of cadmium sulphate. Unlike the zinc halides, zinc sulphate when heated does not ionize the surrounding gas.

L. Kahlenberg's values [21] for the eq. **electrical conductivity** of aq. soln. of zinc sulphate with one eq. of salt in v litres of water, are:

v	0·25	1	4	16	128	256	1024	2048	4096
$\lambda_0°$	7·1	16·3	24·7	32·2	47·5	52·9	61·0	64·4	65·4
$\lambda_{95}°$	—	64·2	87·8	123·2	202·9	232·1	268·4	277·6	—

and for v=8192, $\lambda_0°$=65·9. Other measurements have been made by F. Kohlrausch and co-workers, H. C. Jones and co-workers, C. Freund, C. Heim, H. V. Tartar and H. E. Keyes, A. Smits, J. Tollinger, N. Tarugi and G. Bombardini, G. Jäger J. A. Ewing and J. G. MacGregor, E. Becker, E. N. Horsford, W. von Beetz, E. H. Marié-Davy, J. H. Long, S. Arrhenius, etc. L. Kahlenberg's values for the conductivity of soln. of cadmium sulphate are:

v	0·25	1	4	16	128	256	1024	2048	4096
$\lambda_0°$	6·7	15·0	21·3	29·5	45·6	50·5	59·4	62·4	63·4
$\lambda_{95}°$	—	52·5	74·6	109·7	185·6	225·1	300·1	357·0	—

Other measurements have been made by O. Grotrian, C. J. J. Fox, F. J. Wershoven, N. Tarugi and G. Bombardini, H. C. Jones and co-workers; F. Kohlrausch and co-workers, G. Vicentini, etc. The effect of *temperature* on the conductivity of soln. of zinc sulphate has been studied by W. von Beetz, F. Kohlrausch, C. Heim, E. Cohen, J. Trötsch, and L. Grossmann. L. Kahlenberg's values for 0° and 95° are indicated above. H. C. Jones and A. P. West give for the temp. coeff. of the conductivity of soln. of zinc sulphate of dilution v:

v	2	8	16	32	128	512	1026	2048	8192
0°–15°	0·999	1·44	1·61	1·84	2·61	3·36	3·48	3·80	3·93
15°–25°	1·11	1·53	1·84	2·18	2·90	3·78	4·09	4·26	4·20

F. J. Wershoven, and O. Grotrian have studied the effect of temp. on the conductivity of soln. of cadmium sulphate. L. Kahlenberg's values at 0° and 95° are indicated above. The effect of *pressure* on the conductivity of soln. of zinc sulphate has been studied by J. Fink, B. Piesch, F. Körber, K. Rogoyski, O. Stern, and C. Freund. The electrical resistance of soln. decreases between 0° and 18° proportionally with the increase of press. up to 300 atm., but at higher press. the decrease is not so much. A. Hollard found that with less than 2 per cent. of dil. *sulphuric acid* in the soln. of zinc sulphate, the conductivity is increased; but with 3 per cent. of acid, the conductivity does not change. J. Kendall and co-workers measured the conductivity of zinc sulphate in anhydrous sulphuric acid. C. Lüdeking, and S. Arrhenius studied the effect of *gelatine*, and found no change; B. von Tietzen-Hennig studied the effect of gelatine and of *calcium sulphate*; H. Wolf, the effect of *acetic acid*, *alcohol*, and *tartaric acid*; S. Arrhenius, of methyl and ethyl alcohols, *ether*, and *acetone*; E. Wiedemann, of *glycerol*; E. Rimbach and O. Weber, of *lævulose*; and B. Sabat, of *radium*. A. A. Noyes studied the effect of *thallous chloride* on the conductivity of soln. of cadmium sulphate. R. Luther measured the conductivity of soln. of zinc and cadmium sulphates in methyl and ethyl alcohols. N. Isgarischey studied the polarization of soln. of zinc sulphate in the presence of gelatine, gum, and *sucrose*.

The **transport numbers** of zinc sulphate in aq. soln. have been investigated by J. F. Daniell and W. A. Miller, W. Hittorf, A. Chassy, J. Moser, S. Lussana, P. Straneo, G. Kümmell, and R. Gans; and of soln. of cadmium sulphate by C. L. Weber, A. Chassy, V. Gordon, G. Kümmell, B. D. Steele, H. Jahn, and S. Goldlust. A. Mutscheller measured the velocity of the ions in soln. of gelatine containing different conc. of zinc sulphate. G. N. Lewis and M. Randall calculated the activity coeff. of the ions of cadmium sulphate. The percentage **degree of ionization** α of soln. of zinc sulphate, was calculated from the electrical conductivity by H. C. Jones to be:

v	2	8	16	32	128	512	204·8	4096
α at 0°	26·1	36·9	43·6	50·7	65·5	82·9	96·8	100·0
α at 65°	—	28·7	—	39·1	54·4	72·7	87·4	100·0

S. Arrhenius, S. Labendzinsky, H. Wolf, W. Hallwachs, G. N. Lewis and G. A. Linhart, and H. C. Jones and A. P. West also studied the ionization of zinc sulphate

soln. H. C. Jones and F. H. Getman obtained for a mol of $CdSO_4$ in v litres of water :

v	0·80	1·00	1·14	1·60	2·00	4·00	8·00	16·00
α	14·8	19·6	22·8	23·9	27·9	34·0	40·8	48·6

M. Chanoz, P. Godlewsky, G. N. Lewis and G. A. Linhart,[22] and S. Labendzinsky also investigated the ionization of soln. of cadmium sulphate.

The **electromotive force** in millivolts between two soln. of zinc sulphate Zn | $m$$ZnSO_4$,$n$$ZnSO_4$ | Zn with the percentage concentrations m and n, was found by J. Moser to be :

	$n\rightarrow$	15	30	45	60
m	1	18	22	28	36
	15	—	5	13	21
	30	—	—	7	17
	45	—	—	—	9

C. R. A. Wright and C. Thompson made similar determinations mainly with more dil. soln. of zinc sulphate ; E. Paschen, and A. Smits also worked on this subject. V. Karpen studied the e.m.f. of a cell with zinc : aq. soln. amyl alcohol : $ZnSO_4$. J. Mathieu, M. Chanoz, and C. R. A. Wright and C. Thompson studied the e.m.f. between soln. of cadmium sulphate of different conc. S. Labendzinsky studied the e.m.f. of zinc in aq. soln. of sulphate against a normal calomel electrode, and the effect of temp. was investigated by K. A. Brander, A. Ebeling, E. Bouty, A. Gockel, A. Hagenbach, J. Gill, H. L. Bagard, and H. Jahn. R. Ramsey, and R. Gans investigated the effect of press. ; and H. Jahn the heat of absorption at the anode during electrolysis. B. Neumann, and A. Gockel investigated the e.m.f. of cadmium in soln. of cadmium sulphate. The thermodynamics of *Daniell's cell*, Zn : $ZnSO_4$, $CuSO_4$: Cu, has been studied by W. Nernst, and by E. Cohen and co-workers ; E. Paschen found the e.m.f. decreases continuously with increasing conc. of the zinc sulphate soln. ; E. Cohen measured the internal resistance of Daniell's cell which fell from 420·2 ohms at 48° to 347·2 ohms at 64°—W. H. Preece's and H. S. Carhardt's data are inaccurate ; W. Block also found the temp. coeff. of the cell. H. S. Carhardt found the e.m.f. of *Clark's cell*, $Zn_{amalgam}$ $ZnSO_4$ | $ZnSO_4$, Hg_2SO_4 | Hg, changed with the conc. of the soln.

Sp. gr. at 20°	1·036	1·036	1·096	1·206	1·293	1·383	1·429
E.m.f.	1·4850	1·4777	1·4724	1·4605	1·4540	1·4444	1·4380

The effect of temp. and conc. was also studied by G. Platner, and by H. T. Barnes and co-workers. The e.m.f. at $\theta°$, according to W. Jäger and K. Kahle, is $1·4328—0·00119(\theta—15)—0·000007(\theta—15)^2$ between 0° and 30° ; and, according to H. L. Callendar and H. T. Barnes, between 15° and 39°, the e.m.f. at $\theta°$ less the e.m.f. at 15° is $0·001200(\theta—15)—0·0000062(\theta—15)^2—0·00006(\theta—15)^3$. L. Clark gave 1·4378 for the e.m.f. of the cell at 15° ; R. T. Glazebrook and S. Skinner, 1·4344 ; K. Kahle, 1·4322 ; W. Jäger and K. Kahle, 1·4328—1·4329, and H. S. Carhart and K. E. Guthe, 1·4333. The mean value is 1·4334. The e.m.f. of the cell at the transition point of hepta- to hexa-hydrated zinc sulphate is 1·4005. The cell Cd | $CdSO_4$, Hg_2SO_4 | Hg was studied by S. Czapski in 1884, and employed with amalgamated cadmium by E. Weston as a standard cell in 1892, in place of Clark's standard cell. The variation of the e.m.f. of *Weston's cell* with temp. is such that at $\theta°$ the e.m.f. is $1·0186—0·000038(\theta—20)—0·00000065(\theta—20)^2$. The cell has been investigated by G. A. Hulett, R. A. Lehfeldt, E. Cohen and co-workers, H. von Steinwehr, J. Henderson, etc. E. A. Wolff gave for the e.m.f., E, of Weston's normal element at $\theta°$ between 0° and 40° with 12·5 per cent. cadmium amalgam as negative pole, $E=E_{20}—0·0000406(\theta—20)—0·00000095(\theta—20)^2+0·00000001(\theta—20)^3$. W. Jäger and R. Wachsmuth gave $E=E_{20}—0·000038(\theta—20)—0·00000065(\theta—20)^2$. The latter agrees better with E. Cohen and J. J. Wolters' observations. R. Ramsey has studied the effect of press. on the cell. Certain

irregularities in the Weston's cell have been attributed by P. Kohnstamm and E. Cohen to a change in the cadmium sulphate at 15°, but H. von Steinwehr could find no evidence of a transition point between 13·7° and 25°; H. C. Bijl attributed the irregularity to a change in the nature of the cadmium amalgam with a certain conc. of cadmium. J. Obata and Y. Ishibash studied the standard cadmium cells, and found that the acidity of the soln. had no influence on the temp. coeff.

E. Bouty, and A. Hagenbach measured the **thermoelectric force** of cadmium against cadmium sulphate. Heptahydrated zinc sulphate was found by M. Faraday,[23] and G. Meslin to be diamagnetic; J. Grailich and V. von Lang said it is strongly diamagnetic, and J. Plücker, feebly diamagnetic. H. Knoblauch and J. Tyndall studied the magnetic orientation of the crystals. G. Quincke found the **magnetic susceptibility** of aq. soln. of zinc sulphate, when that of a vacuum is zero, to be $-0{\cdot}27\times10^{-6}$ units between 18° and 20°; G. Meslin gave $-0{\cdot}53\times10^{-6}$ units. G. Quincke also found the diamagnetization constant of soln. of sp. gr. 1·4393 to be $-4{\cdot}701\times10^{-10}$; and the atomic magnetism, $-0{\cdot}0623\times10^{-10}$.

The aq. soln. of zinc and cadmium sulphates are feebly hydrolyzed when the soln. of these sulphates are tested with *herapathite*, *i.e.* quinine sulphatoperiodide. M. C. Lea[24] found no free sulphuric acid, and he attributed the reddening of litmus to a diminution in the dissociation of the litmus salt. J. A. Hedvall and J. Heuberger studied the reaction between zinc sulphate and magnesia or the alkaline earths.

J. H. Long measured the **hydrolysis** of soln. of zinc sulphate from the action of the salt on cane sugar; S. E. Moody from the action of potassium iodide and iodate; and H. G. Denham from measurements of the conc. of the H·-ions. The last-named showed that a state of equilibrium is assumed very slowly, and requires almost a month; as a result, the change in the degree of hydrolysis with a rise of temp. is not reversed directly on cooling, so that a state of *super-hydrolysis* appears. H. Ley calculated the hydrolysis of a $\frac{1}{16}$ molar soln. to be 0·03 per cent.; and G. Carrara and G. B. Vespignani found 0·0075 per cent. for a $\frac{1}{2}$ molar soln. of zinc sulphate, and 0·017 per cent. for a 0·1*N*-soln. of cadmium sulphate. A. Colson studied the activity of aq. soln. of zinc sulphate; and he inferred that the salt has the formula $(ZnSO_4)_2$, and in aq. soln., the formula $HSO_4.Zn.O.Zn.HSO_4$. A number of **basic zinc sulphates** has been reported, but there is little evidence to show that any of these are chemical individuals. Similar remarks apply to the so-called **basic cadmium sulphates.** V. Hassreidter,[25] and H. Pommerenke stated that basic zinc sulphate is formed during the roasting of zinc blende; and A. J. J. van de Velde and C. E. Wasteels by the action of zinc on a soln. of cupric sulphate. F. O. Doeltz and C. A. Graumann claims that the alleged basic sulphates appear to be nothing more than mixtures of zinc oxide and zinc sulphate.

According to R. Schindler, a soln. of **zinc monoxysulphate,** $2ZnO.SO_3$ or $ZnSO_4.ZnO$, is obtained when a conc. soln. of the sulphate is left for a long time in contact with metallic zinc or zinc oxide; and also by precipitating the oxide from half of a conc. soln. of the sulphate, and mixing the precipitate with the other half of the soln. The soln. yields small crystals on evaporation; the salt is decomposed by rapid boiling, slow evaporation, or by digestion with a large proportion of water, and zinc trioxysulphate is precipitated; and it gives a precipitate with tincture of galls. According to M. Athanasesco, small colourless transparent crystals of the monohydrate, $2ZnO.SO_3.H_2O$, or $(ZnOH)_2SO_4$, are obtained by heating to 200°–250°, in a sealed tube, a mixture of 3 parts of $ZnSO_4$ with 100 of water.

A. Vogel prepared dihydrated **zinc trioxysulphate,** $ZnSO_4.3ZnO.2H_2O$, by heating zinc sulphate, until it is partially decomposed, and then boiling the residue with water; by boiling an aq. soln. of zinc sulphate with metallic zinc or zinc oxide; and by precipitating a conc. soln. of zinc sulphate with a small proportion of potassium hydroxide, and boiling the washed precipitate with water. According to O. B. Kühn, if too much alkali be used, a more basic salt will be formed. In all

cases the soln. is filtered hot, and the salt separates as the soln. cools. R. Schindler prepared this salt as indicated above. The opaque scales (A. Vogel) or four-sided needles (R. Schindler) lose water between 100° and 125° without melting or crumbling to pieces, and at a low red heat, the salt is decomposed and the zinc sulphate can be leeched out with water. According to O. B. Kühn, the salt is sparingly soluble in hot or cold water, but soluble in a boiling soln. of zinc sulphate. If the material be dried at ordinary temp., R. Schindler's analysis corresponds with the *decahydrate* $ZnSO_4.3ZnO.10H_2O$; and if dried at 100°, with the *dihydrate* $ZnSO_4.3ZnO.2H_2O$; O. B. Kühn's and T. Graham's analyses correspond respectively with $4H_2O$ and $8H_2O$. S. J. Thugutt claimed to have made needle-like crystals of the *trihydrate*, corresponding with hydromagnesite in composition, by heating for 31 hrs. at 192°–218° a mixture of 21 grms. of heptahydrated zinc sulphate, 3 grms. of sodium hydroxide, and 30 c.c. of water. A. Werner represents the formula :

$$\left[Zn\left(\begin{matrix}HO\\HO\end{matrix}Zn\right)_3\right]SO_4$$

W. Zubkowskaja claimed this salt to be a true chemical individual. F. Reindel, and J. Habermann made the *pentahydrate* by dropping dil. ammonia into a boiling conc. soln. of zinc sulphate. The white crystalline powder loses a part of the water at 100° and the rest at a higher temp. K. Kraut reported the *hexahydrate* is formed by pouring a soln. of sodium carbonate into an eq. amount of zinc sulphate in soln. ; and M. Athanasesco, the *heptahydrate*, in hexagonal plates, by heating in a sealed tube at 160° a 25 per cent. soln. of zinc sulphate mixed with zinc oxide. F. Reindel made the *octohydrate* by boiling an excess of a soln. of zinc sulphate with ammonia ; and K. Kraut, by boiling zinc oxide with a soln. of zinc sulphate. According to K. Kraut, the hydrate loses up to 12·47 per cent. of water over sulphuric acid ; at 100° in a current of dry air, 18·5 per cent. ; at 200°, 16·62 per cent. ; and at 260°, 23·79 per cent. According to F. Reindel, it decomposes slowly in contact with water, and precipitates basic cupric sulphate from a soln. of cupric sulphate. When the octohydrate is heated with boiling water for six weeks, F. Reindel obtained what he regarded as **zinc heptoxydisulphate**, $9ZnO.2SO_3.12H_2O$, or $2ZnSO_4.7ZnO.12H_2O$, which loses 8·08 per cent. of water at 110°, and 18·43 per cent. at 260°.

S. U. Pickering reported the formation of a hydrated **zinc tetroxysulphate,** $ZnSO_4.4ZnO.nH_2O$, by treating a soln. of a mol of $ZnSO_4$ in 100 litres of water with the necessary amount of sodium carbonate ; and S. E. Moody prepared the tetrahydrate by the incomplete hydrolysis of a soln. of zinc sulphate with potassium iodide and iodate. R. J. Kane claimed that when zinc diamminosulphate, $ZnSO_4.2NH_3.H_2O$, or $ZnSO_4.2NH_3$, is treated with water, decahydrated **zinc pentoxysulphate,** $6ZnO.SO_3.10H_2O$, or $ZnSO_4.5ZnO.10H_2O$, is formed as a white powder. R. Schindler obtained what he regarded as dihydrated **zinc heptoxysulphate,** $8ZnO.SO_3.2H_2O$, or $ZnSO_4.7ZnO.2H_2O$, by adding water to a conc. soln. of the monoxysulphate. The dried precipitate does not absorb carbon dioxide from air ; when kept in a soln. of normal zinc sulphate it forms the trioxysulphate ; and it is decomposed by gentle ignition into a mass from which water extracts zinc sulphate.

F. Stromeyer [26] prepared what is regarded as hydrated **cadmium monoxysulphate,** $CdSO_4.CdO.H_2O$, by the ignition of monohydrated cadmium sulphate ; O. B. Kühn by treating one-third of a soln. of cadmium sulphate with potassium hydroxide, and boiling the precipitate with the remaining two-thirds ; J. Habermann, by dropping aq. ammonia into an aq. soln. of cadmium sulphate ; B. Grützner, by warming a dil. soln. of cadmium sulphate with hexamethylenetetramine ; and M. Athanasesco, by heating 3 parts of cadmium sulphate with 100 parts of water in a sealed tube at 200°–250°. The last-named process furnishes small colourless monoclinic or triclinic needle-like crystals. The product is sparingly soluble in water, and separates from that soln. in scaly crystals. S. U. Pickering made what he regarded as $4CdO.SO_3.nH_2O$, that is, **cadmium trioxysulphate,** $CdSO_4.3CdO.nH_2O$, by adding a small proportion of sodium carbonate to a soln. of cadmium sulphate.

According to J. A. Arfvedson,[27] anhydrous zinc sulphate is reduced when heated in a current of **hydrogen,** forming zinc oxysulphide. E. Schüler found that anhydrous cadmium sulphate is reduced to cadmium, and cadmium sulphide, but no oxysulphide is formed. P. Klobb found anhydrous zinc sulphate is slowly dissolved by cold **water,** and rapidly by hot water. The solubility of zinc and cadmium sulphates in water has been previously discussed. T. Graham found the anhydrous salt unites with water with the development of heat—*vide* heat of soln.—and R. Brandes, and H. V. Blücher noted that when exposed to air, a mol of the sulphate absorbs nearly seven mols of water. For the hydrolytic action of water on zinc and cadmium sulphates, *vide supra.* G. J. Mulder stated that a sat. soln. of zinc sulphate is partially decomposed by water at about 40° ; and above this temp., when an excess of the solid salt is present, a basic salt is precipitated, and the soln. becomes acidic.

An interesting experiment illustrating the increased hydrolysis which occurs with temp. is due to A. Gunn. Aq. ammonia (sp. gr. 0·88) is added drop by drop to a soln. of 0·2 grm. of zinc sulphate in 5 c.c. of water until two drops above that required to redissolve the precipitate have been added ; 10–12 drops of 10 per cent. sodium phosphate soln. and 5 c.c. of water are added. This soln. is clear ; it becomes opaque if a test-tube containing the liquid be heated to 100° ; and it becomes clear on cooling. The effects can be reproduced a number of times until the loss of ammonia prevents the clearing of the turbid precipitate.

At 18°, 0·65 grm. of anhydrous zinc sulphate was found by C. A. L. de Bruyn to be dissolved by 100 grms. of absolute **methyl alcohol,** and 59 grms. of heptahydrated zinc sulphate ; 100 grms. of 50 per cent. methyl alcohol dissolve 15·7 grms. of the heptahydrate at 16°, and 5·5 grms. at 0°. V. Augur found that methyl alcohol is decomposed, forming a little basic sulphate. H. Schiff found that 10, 20, and 40 per cent. **ethyl alcohol** dissolves respectively 51·1, 39, and 3·45 per cent. of heptahydrated zinc sulphate. R. Luther also found cadmium sulphate is soluble in methyl and ethyl alcohols ; while A. Neumann found it to be insoluble in **ethyl acetate.** According to A. M. Ossendowsky, and M. Klever, 100 grms. of **glycerol** dissolve 35 grms. of zinc sulphate at 15·5°. According to O. Aschan, 100 grms. of 95 per cent. **formic acid** dissolve 0·06 grm. of cadmium sulphate at 18·5°. M. C. Schuyten found that an aq. soln. of zinc sulphate gives a precipitate when treated with **chlorine ;** and with **bromine** or **iodine,** a substitution occurs. R. J. Kane stated that anhydrous zinc sulphate is dissolved but not decomposed by **hydrochloric acid ;** but C. Hensgen found **hydrogen chloride** decomposes zinc sulphate at 225° to 250°. A. B. Prescott found that when a gram of zinc or cadmium sulphate is evaporated to dryness with 4·035 grms. of hydrochloric acid containing 1·251 grms. of HCl, respectively 4·007 and 0·017 grm. of chloride are formed. C. Baskerville found that cadmium sulphate when heated to 150° in a stream of hydrogen chloride furnishes a product with the composition $3CdSO_4.4H_2O.4HCl$; at 200°, $2CdSO_4.8HCl$; and with a more prolonged action at 200°, or with a shorter heating at a higher temp., cadmium chloride is formed. The **cadmium sulphate hydrochlorides** are very deliquescent.

L. N. Vauquelin,[28] and J. L. Gay Lussac found that when a mixture of zinc sulphate and **sulphur** is heated to redness in an earthen retort, sulphur dioxide is evolved, and a mixture of zinc sulphide and sulphate remains ; and H. Rose found that zinc sulphate is converted into sulphide when heated with sulphur in a stream of hydrogen. According to G. Vortmann and C. Padberg, soln. of zinc and cadmium sulphates are not altered when boiled with sulphur ; but K. Brückner found that zinc sulphate is converted into the sulphide with the evolution of sulphur dioxide, when the salt is triturated with sulphur. F. von Kobell obtained by chance monoclinic crystals of **zinc hydrosulphate,** $ZnH_2(SO_4)_2.8H_2O$, or $ZnSO_4.H_2SO_4.8H_2O$, from a sulphuric acid soln. of zinc sulphate. The salt is sparingly soluble in cold water and readily soluble in hot water ; it fuses when heated, giving off water and sulphuric acid. R. Engel measured the solubility of cadmium sulphate in sulphuric acid at 0°, and found in grams per 100 grms. of water :

H_2SO_4	0	1·90	6·18	13·78	21·23	23·34	26·38	35·06
$CdSO_4$	74·61	72·87	65·03	52·73	42·52	38·56	34·07	23·96
Sp. gr.	1·609	1·591	1·545	1·476	1·435	1·421	1·407	1·379

F. Bergius reported some inaccurate data for the solubility of zinc sulphate in **sulphuric acid** at 25°; J. Kendall and A. W. Davidson measured the solubility, and found:

Per cent. $ZnSO_4$	0·20	0·30	0·41	0·45	0·41	0·45	0·52	0·67
F.p.	28·4°	40·1°	46·4°	49·2°	66·4°	78·0°	94·8°	128·6°
Solid phases	$ZnSO_4.nH_2SO_4$				$ZnSO_4$ (?)			

When zinc or cadmium sulphate is heated in a sealed tube with **sodium thiosulphate,** J. T. Norton found sulphur and the metal sulphide are formed.

According to J. L. Gay Lussac, when zinc sulphate, mixed with **carbon,** is heated to dull redness, sulphur dioxide and carbon dioxide are evolved in the proportion 2 : 1 by vol., and a mixture of zinc oxide, and traces of the sulphide remain; and at a still higher temp. some zinc is formed. If the mixture of zinc sulphate and carbon be rapidly heated to whiteness in a porcelain retort, sulphur dioxide alone is evolved at first, then follows carbon monoxide with a little of the dioxide, and the residue is zinc sulphide. H. O. Hofman and co-workers found the speed of the reaction between zinc sulphate and carbon increases as the temp. rises from 400° to 528°, and at the latter temp., the sulphate begins to be directly converted into the sulphide. According to K. Stammer, **carbon monoxide** converts red-hot zinc sulphate into the oxide. A. Christoff found that a litre of a 2*N*-soln. of zinc sulphate at 15° and 720 mm. press., absorbs 0·072 grm. of **carbon dioxide**. G. Gore noted a rise of 0·41° in 3 mins. when 6·5 grms. of powdered and dry **silica** were added to 50 c.c. of a 10 per cent. soln. of zinc sulphate.

According to J. Matuschek, when a mixture of dry zinc sulphate and **sodium nitrite** is shaken, nitrous oxide is formed. E. P. Alvarez obtained a white precipitate by adding **sodium pernitrate** to a soln. of zinc or cadmium sulphate. When zinc sulphate is heated in a stream of **ammonia,** W. R. Hodgkinson and C. C. Trench obtained approximately mol. proportions of zinc oxide and sulphide. For the complex salts with ammonia, *vide infra.* If a soln. of zinc sulphate is treated with **cupric hydroxide,** and gradually heated, the colour suddenly changes from blue to bluish-green between 70° and 75°, and, after boiling a few minutes, the soln. contains no copper. According to A. Recoura, the precipitate is a complex, $ZnSO_4.3CuO.aq.$ According to D. Vitali, cadmium hydroxide is formed when a soln. of cadmium sulphate is treated with **silver oxide**. K. Brückner reduced zinc sulphate by heating it with powdered **magnesium,** and found sulphur, sulphur dioxide, magnesia, and thiosulphate were formed. K. A. Hofmann and K. Höschele found that when fused with **magnesium chloride,** volatile zinc chloride is formed. C. Paal and C. Amberger studied the action of zinc sulphate on **fats**; E. Rimbach and O. Weber, and L. Kahlenberg and co-workers, on **sugar**; C. J. Levites, on **starch**; and A. Bömer, on **albumen.**

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§ 17. The Ammino- and Complex Salts of Zinc and Cadmium Sulphates

H. Rose [1] found that anhydrous zinc sulphate rapidly absorbs ammonia gas, much heat is evolved, and the mass swells up and crumbles to a white powder which retains nearly 34 per cent. of ammonia, and corresponds with $ZnSO_4.5NH_3$, **zinc pentammino-sulphate.** The product gives off ammonia when heated to redness, and gives a small sublimate of ammonium sulphate; the residue is no longer soluble in ammonia. The pentammino-salt dissolves in water with the partial precipitation of zinc hydroxide. H. Rose similarly prepared **cadmium hexammino-sulphate,** $CdSO_4.6NH_3$, which is decomposed by water. F. Isambert measured the dissociation press. up to 100°, and he found at 48·5°, 368 mm.; at 51·5°, 4·39 mm.; and at 100°, 1374 mm. The break in the curve near 100° corresponds with **cadmium diammino-sulphate,** $CdSO_4.2NH_3$; above 100°, the compound is completely decomposed. F. Ephraim gave 19° for the temp. of decomposition of **zinc hexammino-sulphate.**

According to A. Gunn, a soln. of zinc ammino-sulphate can be prepared by dissolving about 0·2 grm. of zinc sulphate in 5 c.c. of water; and adding aq. ammonia (sp. gr. 0·880), drop by drop, until two drops have been added in excess of that required to redissolve the precipitate; 10–12 drops of a 10 per cent. soln. of sodium phosphate are then added, and 5 c.c. of water. The soln. is quite clear, but, when heated, the liquid becomes opaque, and the turbidity increases as the temp. rises until a thick curdy precipitate falls. This result is due to the dissociation of the soluble ammino-sulphate. When the vessel containing precipitate and mother liquid is warmed, the precipitate is quickly dissolved leaving the soln. as clear as at first. The precipitation by heating and re-solution on cooling can be repeated many times if care be taken to prevent the loss of ammonia. The equilibrium conditions in soln. containing zinc sulphate, water, and ammonia have been studied by W. Zubkowskaja. S. Tschumanoff has measured the electrical conductivity of the soln.; and A. A. Blanchard the viscosity of the soln. W. Gaus found the vap. press. of N-NH_4OH in 0·01N-$ZnSO_4$ soln. at 25° is lowered by 0·44 mm., and similarly with cadmium sulphate, 0·52 mm.; he inferred that the

soln. contains 3 or 4 mols of NH_3 per gram-atom of zinc; H. Euler also inferred that the complex cation $[Zn(NH_3)_4]_n$ is present in the soln.; and H. M. Dawson and J. McCrae also showed that in soln. containing a large excess of ammonia, 4 mols of ammonia are united with one mol of zinc sulphate. W. Herz has studied the equilibrium between soln. of cadmium sulphate and ammonia.

According to R. J. Kane, when ammonia is passed into a hot sat. soln. of zinc sulphate, until the precipitate is redissolved, flocculent granules of **monohydrated zinc diammino-sulphate,** $ZnSO_4.2NH_3.H_2O$, are deposited as the soln. cools; and more of the same product is obtained by evaporating the soln. to dryness, or allowing it to stand in a warm place. A gummy mass with the same composition is obtained by heating hydrated zinc tetrammino-sulphate until it begins to melt; if fused for a longer time, it loses its water, and forms what is possibly **zinc diammino-sulphate,** $ZnSO_4.2NH_3$. At a still higher temp. the whole of the ammonia is evolved. When treated with water, zinc tetrammino-sulphate and ammonium sulphate pass into soln., and decahydrated **zinc pentoxysulphate,** $ZnSO_4.5ZnO.10H_2O$, remains undissolved. F. Ephraim gave 185° for the decomposition temp. of **zinc triammino-sulphate.**

G. André reported that when a current of ammonia gas is passed into a cooled soln. of zinc sulphate in aq. ammonia, the soln. becomes opalescent; and if the passage of the gas is discontinued at this point, the liquid separates into two layers. When agitated, the two layers form an emulsion, but they rapidly separate again on standing. If the passage of the ammonia gas is continued, the bulk of the lower layer increases, and deliquescent needles of **trihydrated zinc tetramminosulphate,** $ZnSO_4.4NH_3.3H_2O$, separate. If the lower layer is allowed to remain by itself, it usually does not crystallize, but in some cases large tabular crystals of the same composition as the needles are deposited. When the lower layer is agitated with alcohol, no mixing occurs, but slender needles gradually separate at the junction of the two liquids. If a mixture of crystals and the lower liquid is gently heated at about 20°, the crystals dissolve with evolution of ammonia, and an oily lower layer then separates and gradually increases in volume. At 28° all the crystals have disappeared, and at 36° the liquid becomes homogeneous. The upper layer has a sp. gr. of 0·953 at 8°, and contains 25·69 per cent. of ammonia, and 2·15 per cent. of zinc; the lower layer has a sp. gr. of 1·2714 at 8°, and contains 22·16 per cent. of ammonia, and 13·62 per cent. of zinc. The separation into two layers can be observed with strong aq. ammonia and an aq. soln. of zinc sulphate.

If the soln. employed in the preparation of hydrated zinc diammino-sulphate be evaporated at ordinary temp., R. J. Kane showed that transparent crystals of **tetrahydrated zinc tetrammino-sulphate,** $ZnSO_4.4NH_3.4H_2O$, are formed; and these become opaque, when dried in air, passing into **dihydrated zinc tetrammino-sulphate,** $ZnSO_4.4NH_3.2H_2O$; and when kept between 27° and 38°, another mol of water is evolved and the mass crumbles to a white powder. If kept for a while at 100°, water and ammonia are given off, and the diammino-sulphate is formed as indicated above. The crystals are soluble in water. According to G. Müller, when a sat. soln. of zinc sulphate and ammonia is treated with alcohol, a syrupy liquid is produced which, in time, deposits tetrahedral crystals of the dihydrated tetrammino-sulphate which lose ammonia when exposed to air; if the crystallization occurs during a winter's cold, the tetrahydrate is formed. F. Ephraim gave 98·5° for the decomposition temp. of zinc tetrammino-sulphate.

R. Schindler claimed to have made **tetrahydrated zinc tetrammino-trioxy-sulphate,** $ZnSO_4.3ZnO.4NH_3.4H_2O$, or $4ZnO.SO_3.4NH_3.4H_2O$, by precipitation from a boiling soln. of zinc sulphate supersaturated with ammonia, and continuing the boiling until the liquid no longer smells of ammonia. R. Schindler further found that when alcohol is added to an ammoniacal soln. of zinc mono- or trioxysulphate, small crystals are precipitated in which the proportion of acid : ammonia is less the greater the dilution. A soln. of zinc sulphate is not rendered turbid by the addition of small proportions of water, but with larger proportions of water, the

precipitate of basic sulphate is granular, and with still larger proportions of water, the precipitate is gelatinous. An ammoniacal soln. of zinc sulphate, when exposed to air, deposits zinc tetroxysulphate, and a zinc amminosulphate remains in soln. G. Bonnet obtained a zinc amminoxysulphate with 2·42 per cent. of ammonia, 81·65 per cent. of zinc oxide, and 15·93 per cent. of sulphur trioxide, by diluting an ammoniacal soln. of zinc sulphate with water.

G. André, and H. L. Wells prepared **dihydrated cadmium tetrammino-sulphate,** $CdSO_4.4NH_3.2H_2O$, from an ammoniacal soln. of cadmium sulphate by evaporation; by pouring a layer of alcohol over the soln.; by passing ammonia into the well-cooled soln. F. J. Malaguti and M. Sarzeau obtained **tetrahydrated cadmium tetrammino-sulphate,** $CdSO_4.4NH_3.4H_2O$, by pouring alcohol into an ammoniacal soln. of cadmium sulphate. The yellow crystals are decomposed by water, and give off ammonia when exposed to air. G. Müller prepared short six-sided prisms by a similar process, but they contained $2\frac{1}{2}$ mols of water.

A soln. of eq. proportions of zinc and ammonium sulphates furnishes crystals of **hexahydrated ammonium zinc sulphate,** $ZnSO_4.(NH_4)_2SO_4.6H_2O$. With a great excess of ammonium sulphate, R. Kempf [2] found the yield to be almost quantitative. The double salt was prepared by F. Tassaert, and J. I. Pierre, and the latter's analysis corresponded more closely with the assumption that the crystals are heptahydrated. J. Troeger and E. Ewers made the crystals by digesting freshly precipitated and well-washed zinc hydroxide in a soln. of ammonium sulphate, and evaporating to crystallization. F. Reindel also obtained fine crystals of the salt. G. Wulff studied the rate of soln., and the rate of growth of the crystals; and also the disturbing influence of concentration currents. The transparent, colourless crystals have, according to E. Mitscherlich, the same form as the corresponding ammonium magnesium sulphate. The monoclinic prisms were examined by F. von Kobell, A. Murmann and L. Rotter, J. C. G. de Marignac, and A. E. H. Tutton; and, according to the latter, they have the axial ratios $a : b : c = 0{\cdot}7368 : 1 : 0{\cdot}4997$, and $\beta = 106° 51'$. N. I. Surgunoff found the etched crystals had the symmetry of holohedral forms of monoclinic crystals. H. de Sénarmont studied the optical properties of the crystals. The sp. gr. given by L. Playfair and J. P. Joule is 1·897; by H. Schiff, 1·910; by H. G. F. Schröder, by F. L. Perrot, 1·931; and by A. E. H. Tutton, 1·9308 at 20°/4°. L. Playfair and J. P. Joule found the sp. gr. of the salt dehydrated without fusion to be 2·222; and H. G. F. Schröder, 2·273. A. Murmann and L. Rotter gave 209·5 for the mol. vol., and A. E. H. Tutton, 206·38. When heated, the double sulphate was found by F. Reindel to be converted into anhydrous zinc sulphate. The crystals of the salt have a positive double refraction, and A. E. H. Tutton's values for the three indices of refraction are:

	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
α . . .	1·4858	1·4862	1·4888	1·4914	1·4948	1·4992
β . . .	1·4900	1·4904	1·4930	1·4957	1·4990	1·5036
γ . . .	1·4963	1·4967	1·4994	1·5027	1·5056	1·5102

The raising of the temp. from 20° to 70° lowered these numbers between 0·0013 and 0·0019 unit. F. L. Perrot also obtained concordant values for these constants, and he gave for the refraction eq. 102·70–103·74. C. Borel's values for the dielectric constants are $k_1 = 7{\cdot}56$, $k_2 = 6{\cdot}62$, and $k_3 = 5{\cdot}35$. E. Tobler found that 100 parts of water dissolve:

	0°	10°	13°	15°	20°	30°	45°	60°	75°	85°
$(NH_4)_2Zn(SO_4)_2$.	7·3	8·8	10·0	12·5	12·6	16·5	21·7	29·7	37·8	46·2

J. Locke found a litre of a sat. soln. at 25° has 140·8 grms. of salt. F. Reindel found the aq. soln. has an acid reaction. When treated with sodium persulphate, the nitrogen is oxidized to nitrate.

According to J. Troeger and E. Ewers, a neutral soln. of cadmium sulphate gives a precipitate of cadmium hydroxide when treated with aq. ammonia, but no precipitation occurs if a little ammonium sulphate be present. E. Mitscherlich

first prepared **hexahydrated ammonium cadmium sulphate,** $CdSO_4(NH_4)_2SO_4.6H_2O$, by the spontaneous evaporation of a soln. of equi-molecular proportions of the component salts. H. Rose, and C. von Hauer obtained the double salt in a similar manner; H. Schiff crystallized the salt from hot soln.; and J. Troeger and E. Ewers prepared the crystals by digesting freshly precipitated and well-washed cadmium hydroxide in a soln. of ammonium sulphate, and evaporating to crystallization from the soln. acidified with sulphuric acid. G. André obtained crystals with the composition $CdSO_4.3(NH_4)_2SO_4.10H_2O$ by the prolonged action of cadmium oxide on a soln. of ammonium sulphate; and H. L. Wells, $CdSO_4.3(NH_4)_2SO_4$. According to C. F. Rammelsberg, hexahydrated ammonium zinc sulphate forms monoclinic prisms analogous with the corresponding potassium salt, and with axial ratios $a:b:c=0{\cdot}7431:1:0{\cdot}4945$, and $\beta=107°\ 41'$. A. Murmann and L. Rotter measured the crystal constants. Large crystals are opaque, small ones transparent. H. Schiff found the sp. gr. to be 2·073. A. Murmann and L. Rotter found the mol. vol. to be 215·73. The crystals are stable in air, and effloresce when dried over sulphuric acid. The salt loses all its water of crystallization at 100°, and melts at a higher temp. and loses water and ammonium sulphate, and finally sulphuric acid, leaving behind basic cadmium sulphate. According to C. von Hauer, the salt can be crystallized from water without decomposition. J. Locke found a litre of water dissolves 735 grms. of the anhydrous salt at 25°. F. Rüdorff dialyzed soln. of the salt, and measured the f.p. of the soln.; H. C. Jones and B. P. Caldwell measured the lowering of the f.p. and the electrical conductivity of soln. of the salt.

No compounds of **lithium sulphate** with zinc or cadmium sulphate have been observed. C. F. Rammelsberg [3] failed to make a double salt of lithium and zinc sulphates. According to G. Calcagni and D. Marotta, lithium and cadmium sulphates give a V-shaped fusion curve with a eutectic at 551° with 45 per cent. of the cadmium salt. T. Graham prepared **tetrahydrated sodium zinc sulphate,** $Na_2SO_4.ZnSO_4.4H_2O$, by evaporating in vacuo over conc. sulphuric acid, a mixed soln. of zinc sulphate and sodium hydrosulphate, $NaHSO_4$; and J. Koppel, by melting together eq. proportions of the component salts at 25°. T. Graham stated that the double salt is not obtained from aq. soln. containing zinc and sodium sulphates, for the component salts separated independently from the complex in cold or warm weather. Similar results were obtained if either salt was in excess. Hence, added T. Graham, "sodium sulphate does not displace the saline water of zinc sulphate so easily as potassium sulphate does." On the other hand, C. J. B. Karsten stated that he obtained the double salt by crystallization from a soln. made by adding Glauber's salt to a sat. soln. of zinc sulphate, or zinc sulphate to a sat. soln. of Glauber's salt, or from a mixed soln. of sodium chloride and zinc sulphate. He added that if the mixture be strongly heated and suddenly cooled, the two salts crystallize out separately. C. Tomlinson, C. F. Bucholz, and J. Koppel also obtained the double salt from aq. soln. of the component salts. The last-named found that the temp. of formation is 8·7°, and the cryohydric temp. of a soln. of zinc and sodium sulphates is −8·3°. He also studied the conditions for the formation of the double salt in aq. soln. The double salt is the sole solid phase at 25° when 17·58 and 15·63 per cent. respectively of zinc and sodium sulphates are in soln., and at 40°, when 17·75 and 15·72 per cent. respectively of zinc and sodium sulphates are in soln. W. H. Miller found the monoclinic crystals have the axial ratios $a:b:c=1{\cdot}344:1:1{\cdot}422$, and $\beta=100°\ 22'$. A. Scacchi also studied the crystals. T. Graham said that the double salt is decomposed when dissolved in water. The crystals are about as deliquescent as sodium nitrate in a damp atm. The salt loses its water of crystallization when heated, and fuses at a dull red heat without losing acid fumes, and solidifies when cooled to a white opaque mass.

G. Calcagni and D. Marotta found that the reactions between fused sodium and cadmium sulphates are very different from those reported by H. le Chatelier. The fusion curve shows that three compounds are formed: **trisodium cadmium sulphate,**

$3Na_2SO_4.CdSO_4$, melting at 351°; **sodium cadmium sulphate,** $Na_2SO_4.CdSO_4$, melting at 551°, and having a transformation point at about 496°; and **sodium tricadmium sulphate,** $Na_2SO_4.3CdSO_4$, melting at 746°, and having a transformation point at about 456°. C. von Hauer prepared small crystals of **dihydrated sodium cadmium sulphate,** $Na_2SO_4.CdSO_4.2H_2O$, by crystallization from conc. soln. in the presence of an excess of sulphuric acid. J. Koppel has studied the conditions of existence of this salt in aq. soln. The double salt is the sole solid phase under the following conditions: at 24° when 22·25 and 15·07 per cent. of cadmium and sodium sulphates are in soln.; and at 40°, when 22·89 and 15·65 per cent. of cadmium and sodium sulphates are in soln.

F. R. Mallet [4] claimed to have prepared crystals of **potassium dizinc sulphate,** $K_2SO_4.2ZnSO_4$, by fusing these proportions of the component salts; the cold mass crystallizes in tetrahedrons; fuses at a red heat, and the mass bloats on cooling; adsorbs moisture from the air, and then decomposes. E. Mitscherlich prepared **hexahydrated potassium zinc sulphate,** $K_2SO_4.ZnSO_4.6H_2O$, in the same manner as the corresponding ammonium salt. According to J. I. Pierre's analysis, the salt has 7 mols of H_2O, but this is wrong. H. Gerhart studied the development of the crystals in acid and neutral soln. C. F. Rammelsberg, E. F. Teschemaker, A. Murmann and L. Rotter have published crystallographic measurements of the monoclinic prisms; A. E. H. Tutton gave for the axial ratios $a:b:c=0{\cdot}7413:1:0{\cdot}5044$, and $\beta=104°\ 18'$. The crystals are isomorphous with the corresponding potassium magnesium sulphate. The sp. gr. was found by H. Kopp to be 2·153; by L. Playfair and J. P. Joule, 2·24034 at 4°; by H. Schiff, 2·153; by H. G. F. Schröder, 2·241; by F. L. Perrot, 2·245 (15°); and by A. E. H. Tutton, 2·2458 at 20°/4°. The sp. gr. of the dehydrated salt is given by L. Playfair and J. P. Joule as 2·816; and by H. G. F. Schröder, as ranging from 2·240 to 2·249 if not melted, and from 2·703 to 3·027 when melted and cooled. A. E. H. Tutton gave 196·16 for the mol. vol. I. Traube found a 10 per cent. soln. has the sp. gr. 1·0678 at 15°, and the specific cohesion 14·012. N. van der Wal, and J. M. van Bemmelen and P. H. B. Ingenhoes studied the rate of diffusion of the soln. According to T. Graham, the hexahydrate loses 5 mols of water in vacuo at 25°, and the sixth mol at 121°; J. I. Pierre said at 180°. F. M. Raoult studied the lowering of the f.p. of the soln. G. Bruni gave −1·0° for the cryohydric temp. of the mixture $K_2Zn(SO_4)_2+ZnSO_4$; and −6·6° for the mixture $K_2Zn(SO_4)_2+K_2SO_4$. J. P. Joule and L. Playfair gave 0·00824 for the coeff. of cubical expansion between 0° and 100°. H. Kopp gave 0·270 for the sp. ht. P. W. Bridgman found that up to press. of 12,000 kgrms. per sq. cm., hexahydrated potassium zinc sulphate shows no signs of undergoing a polymeric change; nor does the anhydrous salt at press. up to 12,000 kgrms. per sq. cm., and at room temp., but there is a sharp break in the volume-press. curve at higher temp. This is taken to correspond with the reversible decomposition of the salt. J. Thomsen gave 4·140 Cals. for the heat of formation from $K_2SO_4+ZnSO_4$; for the heat of hydration, $K_2Zn(SO_4)_2+H_2O$, 18·91 Cals. at 18°, and for the heat of soln. of $K_2Zn(SO_4)_2.nH_2O$:

n	0	1	2	3	4	5	6
Heat of soln.	7·909	4·055	0·446	−2·634	−5·010	−9·176	−11·900 Cals.

The crystals of hexahydrated potassium zinc sulphate have a positive double refraction, and A. E. H. Tutton gave for the three refractive indices:

	Li-line	*C*-line	Na-line	Tl-line	*F*-line	*G*-line
α	1·4748	1·4752	1·4775	1·4797	1·4826	1·4866
β	1·4805	1·4809	1·4833	1·4857	1·4889	1·4929
γ	1·4938	1·4942	1·4969	1·4994	1·5027	1·5067

and for a rise of temp. from 20° to 70°, the indices become smaller by about 0·0018. F. L. Perrot made some concordant observations on the indices of refraction. J. H. Gladstone and W. Hibbert found that the mol. refraction for the H_α-, H_β-,

and the Na-lines of a 8·41 per cent. soln. was respectively 95·95, 98·01, and 96·03; and for a 11·94 per cent. soln., respectively 95·77, 98·08, and 95·94. E. Bouty, and J. Trötsch measured the electrical conductivity of aq. soln. of the salt C. Borel gave for the dielectric constant k_2=6·42.

C. F. Bucholz reported that one part of the salt dissolves in 5 parts of cold water; E. Tobler that 100 parts of water dissolve

	0°	10°	15°	25°	36°	45°	50°	58°	65°	70°
Salt . . .	12·6	18·7	22·5	28·8	39·9	51·2	54·0	67·0	81·3	87·9

J. Locke found that a litre of water at 25° dissolves 131·9 grms. of the anhydrous salt.

G. Calcagni and D. Marotta made a thermal analysis of fused mixtures of cadmium and potassium sulphates, and noted the formation of two compounds, **potassium dicadmium sulphate,** $K_2SO_4.2CdSO_4$, melting at 763°, and of **potassium tricadmium sulphate,** $K_2SO_4.3CdSO_4$, melting at 813°. According to E. Mitscherlich, **hexahydrated potassium cadmium sulphate,** $K_2SO_4.CdSO_4.6H_2O$, can be made; and C. von Hauer claimed to have made it, but with difficulty, by saturating a soln. of potassium hydrosulphate with cadmium carbonate, acidifying with sulphuric acid, and evaporating the soln. spontaneously. The salt cannot be obtained by cooling a hot soln., and it is liable to decompose in its own mother liquid with a change of temp. The crystals are said to be efflorescent, and H. Schiff gives 2·438 for their sp. gr. G. Wyrouboff said that the salt may possibly be obtained by crystallization of the soln. below 0°. A. E. H. Tutton did not succeed in making the hexahydrate. By spontaneously evaporating a neutral soln. of the component salts, C. von Hauer obtained crystals of **hemitrihydrated potassium cadmium sulphate,** $K_2SO_4.CdSO_4.1\frac{1}{2}H_2O$. According to G. Wyrouboff, the crystals are formed in aq. soln. between 26° and 64°; by exposing the dihydrate in air; or by heating the tetrahydrate to 120°. According to J. A. Krenner, the monoclinic prisms have the axial ratios $a:b:c$=0·9873 : 1 : 2·0246, and β=104° 42′. G. Wyrouboff gives for the solubility per 100 grms. of water 42·50 at 26°; 42·80 at 31°; 43·45 at 40°; and 44·90 at 64°. G. Wyrouboff made **dihydrated potassium cadmium sulphate,** $K_2SO_4.CdSO_4.2H_2O$, by evaporating a soln. of the components between 16° and 40°, or by exposing the tetrahydrate to air. The plate-like crystals belong to the triclinic system and have axial ratios and angles $a:b:c$ =0·7967 : 1 : 0·4242, and α=89° 25′; β=109° 22′; and γ=88° 26′. J. A. Krenner, O. Mügge, and C. von Hauer also prepared crystals which had a strong negative double refraction, and a feeble dispersion. The sp. gr. is 2·922 at 16°; and the mol. vol. 143. The crystals of the dihydrate lose water when exposed to air and pass into the hemitrihydrate. G. Wyrouboff gave for the solubility in 100 parts of water, 42·89 at 16°; 46·82 at 31°; and 47·40 at 40°. G. Wyrouboff obtained monoclinic plates of tetrahydrated potassium cadmium sulphate, $K_2SO_4.CdSO_4.4H_2O$, by cooling a hot soln. of the component salts, or by evaporating the soln. between 0° and 16°. The axial ratios are $a:b:c$=1·0894 : 1 : 1·2365, and β=102° 59′. The sp. gr. is 2·523. The crystals have a positive double refraction and a feeble dispersion. The crystals effloresce on exposure to air, forming the dihydrate. At 120°, the crystals lose $2\frac{1}{2}$ mols of water and the remainder at 160°, forming the anhydrous **potassium cadmium sulphate,** $K_2SO_4.CdSO_4$.

According to R. Bunsen and G. Kirchhoff, the sulphates of the magnesium family readily form double salts with cæsium and rubidium sulphates. A. E. H. Tutton, and F. L. Perrot prepared **hexahydrated rubidium zinc sulphate,** $Rb_2SO_4.ZnSO_4.6H_2O$, and **hexahydrated cæsium zinc sulphate,** $Cs_2SO_4.ZnSO_4.6H_2O$, in monoclinic prisms by evaporating a soln. of the component salts. A. E. H. Tutton's values for the axial ratios of the rubidium salt are $a:b:c$=0·7373 : 1 : 0·5011, and β=105° 53′, and for the cæsium salt, $a:b:c$=0·7274 : 1 : 0·4960, and β=107° 1′. F. L. Perrot made similar observations. The sp. gr. of the rubidium and cæsium salts, according to A. E. H. Tutton, are respectively 2·591 and 2·875; and, according to F. L. Perrot,

respectively 2·595 and 2·88. The double refraction of both salts is positive. A. E. H. Tutton found for the three indices of refraction of the rubidium salt :

	Li-line.	*C*-line.	Na-line.	Tl-line.	*F*-line.	*G*-line.
α . .	1·4807	1·4811	1·4833	1·4857	1·4886	1·4929
β . .	1·4856	1·4860	1·4884	1·4908	1·4938	1·4980
γ . .	1·4947	1·4951	1·4975	1·5001	1·5033	1·5078

with a diminution of 0·0012 when the temp. rises from 20° to 70°. He also found for the cæsium salt :

α . .	1·4994	1·4998	1·5022	1·5047	1·5079	1·5125
β . .	1·5020	1·5024	1·5048	1·5073	1·5104	1·5151
γ . .	1·5064	1·5068	1·5093	1·5119	1·5152	1·5199

with a diminution of 0·0016 when the temp. rises from 20° to 70°. F. L. Perrot also made concordant observations on these two salts. J. Locke gives for the solubility of the anhydrous salt in a litre of water at 25°, 0·236 grm. of the rubidium salt, and 0·738 grm. for the cæsium salt.

According to C. J. B. Karsten,[5] **cupric sulphate** dissolves slowly in a sat. soln. of zinc sulphate ; but the latter dissolves rapidly in a sat. soln. of cupric sulphate ; and in both cases, the undissolved portion of the added salt is converted into a double salt. E. Mitscherlich found that a double salt crystallizes from a soln. containing an excess of zinc sulphate and the crystals have the form of ferrous sulphate with 7 mols of water of crystallization, while the crystals of the double salt obtained from a soln. containing an excess of cupric sulphate resemble the latter and have 5 mols of water of crystallization. C. F. Rammelsberg stated that in order to get the last-named crystals, for each mol of $ZnSO_4.7H_2O$, at least 5 mols of $CuSO_4.5H_2O$ must be present—C. Weltzien stated 13 mols of $CuSO_4.5H_2O$. C. von Hauer obtained what he regarded as a double salt $(CuSO_4.7H_2O).2(ZnSO_4.7H_2O)$; J. Lefort, J. M. Thomson and W. P. Bloxam, and J. Nicklès, the double salt $(CuSO_4.7H_2O).3(ZnSO_4.7H_2O)$; and W. H. Wollaston, the double salt $(CuSO_4.7H_2O).4(ZnSO_4.7H_2O)$. The mixed crystals, $CuSO_4.2ZnSO_4.28H_2O$, obtained from the copper ores of Chessy, were called *vitriol mixte Chypre*. A. Scott also reported crystals of $CuSO_4.2ZnSO_4.3H_2O$ analogous with $CuSO_4.2FeSO_4.3H_2O$. The minerals *brochantite* of A. Levy ; *brongniartine* of J. J. N. Huot ; *krisurigite* of G. Forchhammer ; and *warringtonite* of N. S. Maskelyne, are more or less impure mixed crystals of zinc and copper sulphates ; they were also analyzed by G. Magnus, P. Berthier, H. Risse, F. Pisani, R. Warrington, G. Tschermak, F. von Kobell, F. Field, J. Domeyko, F. A. Genth, etc. P. A. Favre and C. A. Valson measured the heat developed during the soln. of the mixed crystals in water. E. S. Larsen and M. L. Glenn discussed the *melanterites*, $(Zn, Cu, Fe)SO_4.7H_2O$; and the *chalcanthites*, $(Zn, Cu)SO_4.5H_2O$.

J. W. Retgers found that with soln. of zinc and copper sulphates, rhombic mixed crystals resembling $ZnSO_4.7H_2O$ are produced with up to 2·32 per cent. $CuSO_4.7H_2O$; monoclinic mixed crystals with 16·65 to 34·41 per cent. $CuSO_4.7H_2O$; and triclinic mixed crystals with 16·65 to 34·41 per cent. $CuSO_4.7H_2O$; and triclinic mixed crystals with 92·02 to 100 per cent. $CuSO_4.5H_2O$. The composition of the mixed crystals of one salt with a maximum of the other—*mixing limit*—was shown by H. W. Foote to be a function of the temp. The two salts do not form completely isomorphous crystals between 12° and 56° ; and in soln. yielding two forms of mixed crystals, the proportion of copper sulphate in soln. remains nearly constant, while the proportion of zinc sulphate increases considerably with rise of temp. The subject has also been investigated by R. Hollmann, E. Cohen, W. Stortenbeker, and L. de Boisbaudran—*vide* cupric sulphate. J. W. Retgers believed that no double compound of zinc and copper sulphates has been prepared, but R. Hollmann inferred that the existence of maxima in the vap. press. curves of soln. of the mixed salts corresponds with the existence of soln. of definite double

compounds. A. Étard obtained rose-coloured crystals of a *cupric zinc hydrosulphate*, $2(ZnSO_4.CuSO_4).H_2SO_4$, by heating to 200° a soln. of the constituents in the smallest possible proportion of water, and in large excess of conc. sulphuric acid. Mixed crystals of *triple salts* with zinc, cupric, and ammonium sulphates were studied by H. Vohl, and A. Fock; and mixed crystals of zinc, cupric, and potassium sulphates by A. Bette, and H. Vohl. Mixed crystals of cupric and cadmium sulphates were found by J. W. Retgers to be colourless and monoclinic with 99·45 to 100 per cent. of $CdSO_4.3H_2O$; and blue and triclinic with 98·29 to 100 per cent. of $CuSO_4.5H_2O$.

Several **basic cupric zinc sulphates** have been reported. The mineral *serpierite* occurs in rhombic crystals at Laurium, and was described by A. des Cloizeaux,[6] and E. Bertrand; *cuprogoslarite* occurs as a greenish-blue incrustation on the walls of an abandoned zinc mine at Galena (Cherokee, Kansas) and was described by A. F. Rogers. A. Recoura described as compounds $7ZnSO_4.24CuO.nH_2O$, and $ZnSO_4.3CuO.H_2O$; A. Mailhe, $ZnSO_4.3CuO.5H_2O$, $ZnSO_4.5H_2O$, $2ZnSO_4.3CuO.12H_2O$, and $3ZnO.2CuSO_4.12H_2O$; and A. Larsen, $2ZnO.CuSO_4.21H_2O$. A. Recoura also described **basic cupric cadmium sulphates**, $6CdSO_4.20CuO.nH_2O$, and $CdSO_4.3CuO.nH_2O$; and A. Mailhe, $2CdSO_4.3CuO.8H_2O$, and $2CdSO_4.3CuO.12H_2O$.

J. d'Ans[7] boiled a conc. soln. of potassium and zinc sulphates with calcium sulphate, and rapidly washed the product with a little water, dil. alcohol, and a mixture of alcohol and ether. The dried product had a composition, **dihydrated potassium dicalcium zinc sulphate,** $K_2Ca_2Zn(SO_4)_4.2H_2O$, and he regarded it as a *potassium-zinc-polyhalite*. He likewise prepared **dihydrated potassium dicalcium cadmium sulphate,** $K_2Ca_2Cd(SO_4)_4.2H_2O$, or *potassium-cadmium-polyhalite*. According to G. Klatzo, monoclinic prisms of **beryllium zinc sulphate,** $2BeSO_4.3ZnSO_4.35H_2O$, isomorphous with heptahydrated zinc sulphate, are obtained by crystallization from a conc. soln. of the component salts.

C. J. B. Karsten[8] found zinc sulphate and **magnesium sulphate** crystallize together. W. Stortenbeker found the solubility isotherm shows a continuous isomorphous series. R. Hollmann assumed that double sulphates are formed, but E. Barchet believed that this is not the case. As E. Sommerfeld showed, the question at issue depends on the definition of a chemical individual. H. Dufet, and G. Wyrouboff found the variation in the sp. gr., and prism angle (110) : (1$\bar{1}$0) of mixtures of zinc and magnesium sulphates to be:

$MgSO_4$.	100	78·88	74·44	62·70	57·59	42·80	35·64	18·11	0 %
Sp. gr. .	1·6760	1·7359	1·7472	1·7816	1·7977	1·8415	1·8604	1·9094	1·9600
Angle . .	90° 35′	90° 42·5′	90° 45′	90° 49′	90° 52′	90° 56·5′	90° 59′	91° 06′	91° 12

G. Bruni found the cryohydric temp. of mixtures of the two sulphates to be:

$MgSO_4$ . .	100	69·5	58·8	37·5	19·6	0 molar %
Cry. temp. .	−5·2°	−5·5°	−5·5°	−6·0°	−6·2°	−6·4°

R. Hollmann gave for the vap. press. of mixtures:

$ZnSO_4$ . .	0	20·4	31·2	37·5	40·2	49·4	59·8	71·1	79·0	100 %
H_2SO_4 . .	45·14	46·09	46·60	43·20	44·17	43·31	40·93	41·50	41·04	38·61
Vap. press. .	7·7	8·0	8·2	8·7	8·3	8·7	9·6	9·5	9·5	10·5

E. Barchet determined the relation between the relative proportions of $ZnSO_4.7H_2O$ and $MgSO_4.7H_2O$ in soln. and mixed crystals.

Mixed crystals	$ZnSO_4.7H_2O$ . .	13·41	20·25	28·67	31·29	46·37	49·05	59·65
	$MgSO_4.7H_2O$ . .	86·59	79·59	71·33	68·71	53·63	50·95	40·35
Soln.	$ZnSO_4.7H_2O$ . .	14·47	20·94	33·71	38·12	50·98	53·54	63·94
	$MgSO_4.7H_2O$ . .	85·53	79·56	76·29	61·88	49·02	46·46	36·06

The alleged magnesium zinc sulphates are: (i) $ZnSO_4.MgSO_4.14H_2O$, prepared by J. I. Pierre, which retains 2 mols of its water of crystallization at 200°, but loses it at 250°–260°. H. Schiff gave 1·817 for the sp. gr. R. Hollmann, E. Barchet, C. von Hauer, and M. Schaeuffele have worked on this compound.

(ii) $3ZnSO_4.5MgSO_4.14H_2O$ was also prepared by H. Schiff, who gave 1·770 for the sp. gr. (iii) $ZnSO_4.2MgSO_4.21H_2O$ was prepared by R. Hollmann, and M. Schaeuffele, but E. Barchet denied its existence. H. Schiff also reported **magnesium cadmium sulphate,** $CdSO_4.MgSO_4.14H_2O$, to be formed by evaporating a sulphuric acid soln. of magnesium and cadmium carbonates in eq. proportions. The sp. gr. of the four-sided prisms is 1·982. The salt dried over sulphuric acid has the composition $CdSO_4.MgSO_4.6H_2O$. A. Bette prepared *triple salts* of zinc and magnesium sulphates with ammonium or potassium sulphate. H. Vohl prepared **potassium magnesium zinc sulphate,** $2K_2SO_4.ZnSO_4.MgSO_4.12H_2O$ and **potassium ammonium magnesium sulphate,** with $(NH_4)_2$ substituted in place of K_2. H. Schiff reported *hydrated triple salts*, **ammonium potassium zinc sulphates,** with $(NH_4)_2SO_4 : K_2SO_4 : ZnSO_4 : H_2O$ in the mol. proportions 2 : 3 : 2 : 3 ; 1 : 2 : 1 : 18 ; and 1 : 1 : 1 : 12.

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§ 18. Zinc and Cadmium Carbonates

The term *calamine*—or, in Germany *Galmei*—is supposed to be a corruption of Pliny's *cadmia*. G. Agricola [1] said that the term was derived from *calamus*, a reed, in allusion to the slender stalactitic forms common with *cadmia fornacum*. The *cadmia* of Pliny, and the early writers, included both the silicate and the carbonate, as well as the oxide from the flues of furnaces. The two ores were confounded under the term *lapis calaminaris*, *calamine*, or *galmei*. Some early analyses showed a difference in composition, thus, T. Bergmann showed that a sample from Holywell, which he called *zincum acido aëro mineralisatum*, contained 28 per cent. of carbon dioxide ; M. H. Klaproth, that a sample from Derbyshire contained 33 per cent. of silica ; and B. Pelletier, that a sample from Fribourg (Brisgau), which he called *zeolite of Brisgau*, contained 52 per cent. of silica. J. B. L. Romé de l'Isle distinguished between the crystalline forms of the two species, the one was described as occurring in prismatic crystals with dihedral summits, and the other as scalenohedral like dog's tooth spar, while R. J. Haüy regarded *zinc carbonatée* as an impure calcareous *zinc oxydé*. In 1803, J. Smithson established the difference between the two minerals and he denominated the silicate *electric calamine*, on account of its pyroelectric qualities. In 1807, A. Brongniart called the silicate *calamine*, and the carbonate *zinc carbonatée ;* and in 1732, F. S. Beudant applied the term *smithsonite* to the carbonate. The two minerals were thus clearly distinguished and named. Confusion resulted when H. J. Brooke and W. H. Miller suggested reversing these terms, and when G. A. Kenngott proposed the term *hemimorphite* for the silicate. The carbonate is commonly called *calamine* or *zinc spar* by British mineralogists, and *smithsonite* by American ; while the silicate is commonly called

hemimorphite or *electric calamine* by British mineralogists, and *calamine* by American.

Zinc carbonate occurs in nature as a crystallized botryoidal, stalactitic, granular, or earthy mass. Analyses have been published by J. Smithson,[2] E. Schmidt, W. Elderhorst, H. Risse, P. Berthier, F. von Kobell, M. Long, F. de Marigny, C. J. B. Karsten, F. A. Genth, E. Ludwig, R. Blum, N. Collie, J. A. Tanner, H. Traube, J. Loczka, L. G. Eakins and H. N. Stokes, W. Ortloff, P. Argall, W. H. Miller, J. C. Brauner, C. H. Warren, A. Christomanos, G. Linder, C. F. Rammelsberg, F. Cornu, B. Neumann and E. Wittich, C. R. van Hise, etc. A ferruginous variety has been called *zinc-iron-spar*, or, according to A. Breithaupt, *capnite*, or *kapnite*; a cupriferous variety, *herrerite*; a ferruginous and manganiferous variety, *monheimite*; and a cadmiferous variety, *cadmium-zinc-spar*.

In his essay *De acido aëreo* (Upsala, 1774), T. Bergmann stated that zinc dissolves in carbonic acid, and it forms zinc carbonate. R. Schindler[3] claimed to have made normal **zinc carbonate,** $ZnCO_3$, containing a little water—probably owing to its association with a little hydrated basic zinc carbonate—by precipitating in the cold a soln. of zinc sulphate in ten times its weight of water with an equi-molar proportion of alkali hydrocarbonate. The white powder obtained by drying the washed precipitate was considered by H. Karmarsch, and by J. Lefort to be a basic carbonate. R. Schindler also obtained a granular powder, supposed to be the normal carbonate, by the spontaneous evaporation of a soln. of zinc, zinc hydroxide, or carbonate in carbonic acid. K. Kraut recommended adding a soln. of 140 grms. of potassium hydrocarbonate or of 117 grms. of sodium hydrocarbonate, sat. with carbon dioxide, to a soln. of 100 grms. of heptahydrated zinc sulphate, cooled to 3° or 4°; the precipitate was filtered by suction as rapidly as possible, washed with ice-cold water, and dried by press. H. de Sénarmont made normal zinc carbonate as a crystalline powder, by heating in a sealed tube to 150° an aq. soln. of zinc sulphate and sodium carbonate; or to 160°, an aq. soln. of a zinc salt and sodium hydrocarbonate. G. Rose employed a similar process. L. Bourgeois recommended heating to 100°, in a sealed tube, a mixture of zinc and carbonic acid. P. N. Raikow passed carbon dioxide into water with zinc hydroxide in suspension. A. Schmidt synthesized zinc-iron-spar by mixing precipitated calcium carbonate with a soln. of ferruginous zinc sulphate, and allowing the mixture to stand in the presence of free carbon dioxide. The crystals of gypsum were removed by washing with hot water. H. Rose added an excess of potassium (not sodium) hydrocarbonate to a cold soln. of zinc sulphate, and found that the product washed and dried at 200° had the composition $5ZnCO_3.H_2O$. H. St. C. Deville found that the precipitate obtained from soln. of zinc sulphate and ammonium hydrocarbonate, when allowed to stand with the mother liquid, forms a granular powder of **hemihydrated zinc carbonate,** $2ZnCO_3.H_2O$, which, according to H. Mikusch, is crystalline. A. Belar obtained fine crystals of **monohydrated zinc carbonate,** $ZnCO_3.H_2O$, by allowing soln. of zinc carbonate in ammonium carbonate to stand for three months. The presence of copper carbonate facilitates the crystallization. K. Kraut also made the same hydrate by the action of sodium hydrocarbonate on a soln. of a zinc salt.

F. Stromeyer,[4] and J. F. John precipitated what they considered to be anhydrous **cadmium carbonate,** $CdCO_3$, by adding an alkali carbonate to a soln. of a cadmium salt; but J. Lefort believed the precipitate to be **hemihydrated cadmium carbonate,** $CdCO_3.\frac{1}{2}H_2O$, which lost its water between 80° and 120°. K. Kraut made the hemihydrate by pouring a large excess of ammonium carbonate into a cold soln. of cadmium nitrate. According to H. Rose, cadmium oxide is more readily attacked than zinc oxide by carbon dioxide, and less readily attacked by water. The precipitate obtained by adding sodium carbonate to a soln. of a cadmium salt is washed with difficulty; the precipitate with potassium carbonate approximates closely to that of normal cadmium carbonate, especially if an excess of potassium carbonate is employed, but in every case some basic cadmium carbonate appears to be formed: with cold conc. soln. the precipitate has $Cd(OH)_2 : CdCO_3 : H_2O$ in the proportion 1 : 10 : 2; with cold dil. soln., 1 : 10 : 3; with hot conc. soln.,

6 : 50 : 11 ; and with hot dil. soln., 9 : 50 : 12. A. de Schulten obtained crystals of the normal carbonate by washing with aq. ammonia the precipitate obtained by adding an excess of ammonium carbonate to a conc. soln. of cadmium chloride, and heating the diluted mixture on a water-bath ; or, according to L. Bourgeois, by heating in a sealed tube the amorphous carbonate with ammonium chloride or nitrate and water at 150°–180° ; or with urea at 140°. K. Kraut dropped a soln. of cadmium sulphate into an eq. soln. of sodium carbonate at the b.p., or boiling the precipitate with the mother liquid for an hour.

The **crystals** of zinc carbonate are scalenohedral and isomorphous with the trigonal family of calcites ; according to A. Breithaupt,[5] the axial ratio is $a : c = 1 : 0{\cdot}8062$, and $\alpha = 105° 28'$; similarly, cadmium carbonate was found by A. de Schulten to have the axial ratio $a : c = 1 : 0{\cdot}8363$, and $\alpha = 102° 30'$. A. Belar found monohydrated zinc carbonate forms bipyramids belonging to the rhombic system with $a : b : c = 0{\cdot}8316 : 1 : 0{\cdot}5994$. According to W. L. Bragg, the **X-radiogram** shows the distance apart of the atoms in zinc carbonate to be 1·99 A., and of cadmium carbonate, 2·21 A. Some observations on this subject were made by M. L. Huggins. The **specific gravity** of zinc carbonate, according to J. Smithson, is 4·339 ; W. Haidinger and W. H. Wollaston gave 4·42 ; A. Levy, 4·45 ; C. J. B. Karsten, 4·3765 ; and W. Ortloff, 4·30–4·45—mol. vol. 28·51. The sp. gr. of cadmium carbonate was given as 4·42 at 17° by W. Herapath ; 4·4938 by C. J. B. Karsten ; 4·258 by H. G. F. Schröder ; and 4·960 at 15° by A. de Schulten. The **hardness** of zinc carbonate is near that of apatite—5 on Mohs' scale. This subject was discussed by A. Reis and L. Zimmermann.

F. O. Doeltz and C. A. Graumann [6] found that some carbon dioxide is given off when commercial zinc carbonate is heated to 90° ; the **decomposition** is faster as the temp. rises ; at 144°, the decomposition is rapid ; at 300°, the decomposition is complete in an hour, and in half an hour at 400° or higher. F. O. Doeltz and C. A. Graumann found the decomposition of the native carbonate begins at 137°, and K. Friedrich found that the decomposition of zinc spar begins at 395° ; siderite at 380° ; magnesite at 570° ; and calcspar at 895° ; and that the decomposition of smithsonite is a maximum at 440°. G. Lindner found the **specific heat** of zinc carbonate is 0·1507 between 0° and 100° ; 0·1608, between 0° and 200° ; 0·1706 between 0° and 300° ; and 0·1740 between 0° and 400°. He also found :

	50°	100°	150°	200°	250°
Sp. ht. . .	0·1507	0·1608	0·1706	0·1805	0·1902

so that the sp. ht. increases with rise of temp. and the increase is smaller the higher the temp. According to M. Berthelot, the **heat of formation** of precipitated zinc carbonate is (Zn, C, 3O) = 194·2 Cals., and, according to J. Thomsen, (Cd, C, 3O) = 181·9 Cals., or (Cd, O, CO_2) = 84·93 Cals.

W. Ortloff [7] found the **double refraction** of native crystals of zinc carbonate, like that of other trigonal carbonates, is strongly negative, and the **index of refraction** $\epsilon = 1{\cdot}61766$. E. Goldstein studied the **phosphorescence** of cadmium carbonate under the influence of cathode rays. G. F. Kunz and C. Baskerville found hydrozincite from Algiers gives a **fluorescence** when exposed to ultra-violet light. According to J. Perrin, the particles of zinc carbonate suspended in alkaline soln. are negative ; in acid soln. they are positive ; and in neutral water, they are electrically neutral. A. E. Garrett found the **electrical conductivity** did not rise when the carbonate is heated.

Zinc spar was found by F. Cornu [8] to react distinctly alkaline to neutral litmus. J. von Essen found that a litre of water at 15° dissolves 0·01 grm. of zinc carbonate, and F. Ageno and E. Valla found at 25°, $1{\cdot}64 \times 10^{-4}$ mols or 0·206 grm. per litre. H. J. Smith estimated that if zinc carbonate were not hydrolyzed, its solubility in water at 25° would be $4{\cdot}58 \times 10^{-6}$ mols per litre. R. Fresenius said a litre of cold water dissolves 0·0224 grm. of basic zinc carbonate. R. Schindler found ignited zinc oxide does not absorb carbon dioxide from the atm., but H. W. F. Wackenroder

found that about 8·3 per cent. of carbon dioxide, is taken up if that gas be passed through water with zinc oxide in suspension. F. Jahn also showed that zinc carbonate, zinc hydroxide, and even metallic zinc, are easily soluble in an aq. soln. of carbon dioxide. C. A. Seyler showed that the solubility is a function of the dissolved carbon dioxide. Presumably **zinc hydrocarbonate,** $Zn(HCO_3)_2$, passes into soln. H. J. Smith showed that the solubility of zinc hydrocarbonate in carbonic acid, expressed in mols per litre when the press. of the carbon dioxide is expressed in atm. at 25°, is :

Press. CO_2	4·12	7·64	12·16	19·73	22·56	40·61
Mols H_2CO_3	0·1390	0·2579	0·4103	0·6657	0·7610	1·3701
Mols $Zn(HCO_3)_2$	0·00194	0·00242	0·00278	0·00317	0·00343	0·00445
α	0·909	0·899	0·894	0·888	0·885	0·871
$K \times 10^3$	3·40	3·41	3·35	3·22	3·33	3·48

where α represents the **degree of ionization** of the zinc hydrocarbonate such that $\alpha[Zn(HCO_3)_2]=Fe^{\cdot\cdot}$. Since $[Zn^{\cdot\cdot}][CO_3'']=K_3$, the **solubility product ;** and $[H^{\cdot}][HCO_3']=K_1[H_2CO_3]$; and $[H^{\cdot}][CO_3'']=K_2[HCO_3']$,

$$\frac{\alpha[Zn(HCO_3)_2]}{\sqrt[3]{[H_2CO_3]}}=\sqrt[3]{\frac{K_1K_2}{4K_2}}=K$$

where K is the equilibrium constant for the system. The average value of the equilibrium constant, K, at 25° is 0·00336, and at 30°, 0·00347. From the known values $K=3·36\times10^{-3}$; $K_1=3·50\times10^{-7}$; and $K_2=4·91\times10^{-11}$, it follows that the solubility product of zinc carbonate at 25° is $K_3=21\times10^{-12}$. C. Immerwahr obtained values for the solubilities of zinc and cadmium carbonates, and she studied the action of potassium carbonate on soln. of the chlorides.

J. von Essen found that the solubility of zinc carbonate is raised when *sodium chloride* or *potassium chloride* is also present, and the action of the alkali chlorides on zinc carbonate was studied by A. Cantoni and J. Passamanik. H. Ehlert found that a litre of a 5 per cent. soln. of sodium chloride dissolves 0·02273 grm. $ZnCO_3$; 10 per cent. soln., 0·04564 grm. ; and a sat. soln., 0·13038 grm. ; a litre of a 10 per cent. soln. of *sodium nitrate* dissolves 0·058981 grm. $ZnCO_3$; and a sat. soln., 0·1490 grm. ; a litre of a 10 per cent. soln. of *sodium sulphate* dissolves 0·009313 grm. of $ZnCO_3$; and a litre of a sat. soln., 0·015521 grm. A small proportion of sodium sulphate thus depresses the solubility of zinc carbonate while a large proportion raises the solubility. A. Cantoni and J. Passamanik showed that the decomposition of zinc carbonate by alkali chlorides is small; it is larger with ammonium chloride, and with increasing temp. and conc. of the soln. W. O. de Coninck found a small reaction between a soln. of sodium chloride and zinc or cadmium carbonate in sunlight. A. Frebault and A. Destrem found zinc carbonate is decomposed by a soln. of *sodium phosphate.*

W. Eidmann found that zinc carbonate is insoluble in **acetone ;** A. Naumann, that cadmium carbonate is insoluble in **ethyl acetate ;** P. Sabatier, that zinc carbonate reacts with **nitrodisulphonic acid,** forming zinc sulphate ; W. Ipatjeff, that zinc carbonate reacts with **acetic acid,** forming ketone, water, and carbon dioxide ; and W. Löb studied the reaction with **formaldehyde,** etc. L. Naudin and F. de Montholon found that zinc carbonate is completely converted by **hydrogen sulphide** into zinc sulphide. M. Kohn noted that precipitated cadmium carbonate precipitates ferric salt soln. in the cold completely, while chromic, uranyl, and aluminium nitrates are but incompletely precipitated.

When zinc salts in soln. are precipitated by alkali carbonates, the products are unstable and of variable composition ; and as a result, a large number of **basic zinc carbonates** have been reported. A sat. aq. soln. of potassium or ammonium carbonate gives a precipitate with zinc salts which is soluble in an excess of the precipitant, presumably, said C. Arnold,[9] by forming a soluble basic zinc carbonate. H. Mikusch believed that only one basic carbonate exists as a stable chemical

individual, and that it is represented by $5ZnO.2CO_2.4H_2O$; and he added that all the other reputed basic zinc carbonates are solid soln. of zinc hydroxide, and normal zinc carbonate. In H. Mikusch's experiments, neutral zinc carbonate was progressively hydrolyzed with water at 25°, 50°, and 100°, and the composition of the liquid and solid phases determined from time to time; conversely, zinc carbonate was formed by the progressive action of zinc hydroxide and carbonic acid, and the solid and liquid phases similarly treated. In all cases, sodium acetate was added to the soln. in order to dissolve sufficient carbonate and hydroxide to allow of analysis. Analyses of the massive or earthy mineral *hydrozincite*—and the varieties *zinc bloom*, *marionite*, *zinconite*, and *cagamite*—by J. Smithson; C. J. B. Karsten; C. Schnabel; T. Petersen and E. Voit; A. Terreil; W. K. Sullivan; G. Bonnet; A. Goebel; W. Elderhorst; C. F. Rammelsberg, G. Cesaro, A. Cossa, V. von Zepharovich, K. Kraut, and A. F. Rogers, show that the composition ranges between $ZnCO_3.2Zn(OH)_2.nH_2O$ and $3ZnCO_3.Zn(OH)_2.3H_2O$. C. Perrier showed that zinc carbonate is also associated with the malachite of Chessy.

R. Schindler reported **dihydrated zinc heptoxycarbonate,** $ZnCO_3.7ZnO.2H_2O$, and **dihydrated zinc trioxycarbonate,** $ZnCO_3.3ZnO.2H_2O$, to be formed when the corresponding basic zinc sulphate is boiled with a soln. of sodium carbonate. P. A. von Bonsdorff made the tetrahydrate by the action of a stream of carbon dioxide on water with zinc oxide in suspension. E. Dittler states that it is doubtful if there is such a compound as **dihydrated zinc dioxycarbonate,** $ZnCO_3.2ZnO.2H_2O$, or $Zn_3(OH)_4CO_3$. According to D. Strömholm, soln. with different proportions of carbon dioxide are in equilibrium with hydrated **zinc trioxydicarbonate,** $2ZnCO_3.3ZnO.nH_2O$. The *monohydrate* was reported by P. A. von Bonsdorff as a result of exposing zinc covered with water to the air. R. Schindler precipitated a soln. of a zinc salt with sodium carbonate, and he found that the product dried at 100° had the composition of a trihydrate: $2ZnCO_3.3ZnO.3H_2O$, which A. Werner formulated

$$\left[Zn\left(\begin{matrix}OH\\OH\end{matrix}Zn\right)_3\right]^{CO_3}_{3CO_3}>Zn$$

According to K. Kraut, the *tetrahydrate* is obtained by pouring a soln. of a zinc salt into a sat. soln. of alkali carbonate; by boiling zinc dust with an excess of carbonic acid; and, according to H. Mikusch, by the hydrolysis of zinc carbonate by boiling water. By the prolonged action of alkali carbonate, the basic salt is finally converted into zinc oxide. H. Rose, and J. B. J. D. Boussingault prepared what he regarded as **monohydrated zinc monoxycarbonate,** $ZnCO_3.ZnO.H_2O$, and K. Feist prepared the same salt by using the soln. warmed to 30°, and drying the product at 100°; the trihydrate is said to be formed by using cold soln. and drying the precipitate in air. C. Perrier represents the composition of the mineral *rosasite* as a basic zinc copper carbonate, $(Zn, Cu)CO_3.Cu(OH)_2$, resembling malachite, with part of the zinc replaced by copper. K. Kraut made **hydrated zinc dioxytricarbonate,** $3ZnCO_3.2ZnO.nH_2O$, by working with dil. soln. at 2°. J. Smithson's, and A. Cossa's analyses of hydrozincite correspond closely with this product; and H. Rose also obtained a similar product by working with very dil. soln. H. Rose reported **monohydrated zinc monoxydicarbonate,** $2ZnCO_3.ZnO.H_2O$, to be formed by the action of a soln. of sodium hydrocarbonate on zinc carbonate; J. Lefort found the product to be trihydrated. C. E. Jansen, J. E. Herberger, and C. Frederking reported **trihydrated zinc trioxydicarbonate,** $2ZnCO_3.3ZnO.3H_2O$, to be formed by the action of sodium carbonate on a soln. of zinc salt; and P. A. Favre, **hexahydrated zinc pentoxytricarbonate,** $3ZnCO_3.5ZnO.6H_2O$, by the action of cold water on zinc ammino-carbonate. R. Hinsberg prepared a basic zinc carbonate by the joint action of carbon dioxide and ammonia at 80° on a conc. soln. of zinc sulphate or chloride. F. Wöhler found the basic salt is deposited in small shining crystals when an aq. soln. of potassium or sodium zincate is exposed to air.

R. Schindler stated that 0·3–0·5 part of basic zinc carbonate dissolves in a litre of water and the salt separates from the soln. when heated, without redissolving on cooling. R. Fresenius said 0·0224 part of the basic salt dissolves in a litre of water. A. Naumann said the basic salt is insoluble in acetone. R. H. Brett, and G. C. Wittstein found the basic salt dissolves readily in a cold aq. soln. of ammonium nitrate or chloride, and the soln., according to L. Thompson, gives off ammonia when heated. A. Terreil said basic zinc carbonate dissolves in a soln. of all the ammonium salts excepting the sulphide. C. Zenghelis found that bright silver foil is dissolved when exposed for 15 days, about 5 cms. away from basic zinc carbonate. M. Kohn found basic zinc carbonate, formed in cold soln., completely precipitates ferric salts, and aluminium or uranium nitrate in cold soln., and chromic salts partly in the cold, and completely when heated.

As previously indicated, H. Rose obtained evidence of the formation of **basic cadmium carbonates,** but the subject was not investigated further. K. Kraut was unable to prepare a basic carbonate of cadmium. Only a very small quantity of cadmium carbonate is dissolved by aq. carbonic acid, even under a press. of several atm. The precipitate obtained by adding cadmium sulphate to a soln. of sodium carbonate consists of cadmium carbonate, $CdCO_3$, mixed with a small quantity of cadmium oxy-sulphate, $2CdO.SO_3$; whilst by adding cadmium nitrate to an excess of ammonium carbonate, the carbonate $CdCO_3.\frac{1}{2}H_2O$ is obtained. O. Schneider found native basic cadmium carbonate in the oxidation-zone of the copper deposits of Otavi (S.W. Africa). He named it *otavite*. It forms white to red, crystalline crusts on the lining cavities; it has a strong lustre, inclined to metallic-adamantine in character. The minute, curved rhombohedra have an angle of about 80°. Analysis shows the mineral to be a basic cadmium carbonate containing 61·5 per cent. of cadmium.

C. Arnold [10] found that ammoniacal soln. of ammonium carbonate gave a precipitate with zinc salt soln., which is soluble in an excess. H. Brandhorst found native calamine dissolves in aq. ammonia only in the presence of ammonium salts. V. Lindt found that raw calamine gives up all its zinc to an ammoniacal soln. of ammonium carbonate, but calcined calamine may not do so if a *zinc ferrite*, $Zn(FeO_2)_2$, is formed. F. de Lassone, and C. Roloff found that zinc filings and zinc oxide readily dissolve in a soln. of ammonium carbonate, with brisk effervescence in the former case. The evaporation of the soln. furnishes white crystals. The sat. soln. gives a white precipitate when treated with acids; and it becomes turbid when treated with an excess of water—because, said G. Bonnet, a compound richer in zinc oxide is precipitated. G. Bonnet also prepared a crystalline powder by digesting zinc oxide with an aq. soln. of ammonium carbonate. According to F. Wöhler, when zinc chloride is dropped into an excess of aq. ammonia, and the product mixed with ammonium carbonate, there are formed, on exposure to air, stellate masses of acicular crystals which are insoluble in water, and have a strong ammoniacal odour; they become turbid when exposed to air, and lose ammonia until a white powder is produced, which when heated evolves water and ammonia, leaving 62·2 per cent. of zinc oxide as residue. P. A. Favre reported that if freshly precipitated zinc carbonate be washed with an aq. soln. of ammonium carbonate, the filtrate deposits rectangular prisms or stellate masses of needles. The composition corresponds with **zinc monammino-carbonate,** $ZnCO_3.NH_3$. With cold water, pseudomorphs of the oxycarbonate $3ZnCO_3.5ZnO.6H_2O$ are formed. The ammino-salt does not change when exposed to air, or when treated with alcohol; and when slowly heated, it gives a sublimate of ammonium carbonate. G. Kassner electrolyzed a soln. of ammonium carbonate with a zinc rod as positive pole, and obtained white crystals of **zinc ammonium hydroxydicarbonate,** $2ZnCO_3.Zn(OH)_2.NH_4OH$, which remain unchanged at 150°. G. Thomas also made some observations on this subject. For the action of ammonium carbonates on cadmium compounds, *vide supra*, cadmium oxide.

Our knowledge of the complex zinc carbonates is imperfect and fragmentary.

R. Schindler [11] reported that the gelatinous precipitate produced by adding an excess of potassium carbonate to a zinc salt soln. at ordinary temp. is a mixture of basic zinc carbonate and a **potassium zinc carbonate.** H. St. C. Deville obtained six-sided prisms of what he regarded as an acid double carbonate, $4K_2O.6ZnO.11CO_2.8H_2O$, by mixing a boiling soln. of zinc chloride with a boiling sat. soln. of potassium carbonate or hydrocarbonate, and allowing the mixture to stand for some time; the product was washed with cold water and dried in vacuo. H. St. C. Deville also prepared a **sodium zinc carbonate,** $3Na_2O.8ZnO.11CO_2.8H_2O$, which K. Kraut considers should be $Na_2O.3ZnO.4CO_2.3H_2O$. It is also considered possible that F. Wöhler's product obtained by exposing a soln. of sodium zincate to the atm. is a sodium zinc carbonate. W. Smith was unable to prepare the compound, $NaO.Zn(NaCO_3)$, reported by F. Wöhler to be produced when a soln. of sodium carbonate acts on zinc with the escape of hydrogen, for, with a hot soln., a white deposit consisting mainly of zinc oxide is formed, and the filtrate contains no zinc. It is, however, possible that with a cold soln. a compound is slowly produced which is decomposed by heat. H. W. F. Wackenroder, as previously indicated, found that zinc oxide is not attacked by a boiling soln. of sodium carbonate. The so-called *aurichalcite* is regarded as a native form of *zinc cupric carbonate*, or as a mixture of the basic carbonates of these elements. This is confirmed by the analyses of S. L. Penfield, T. Böttger, A. Connell, A. Delesse, A. Belar, J. H. Collins, E. Jannetaz, and L. Michel. C. Perrier's analysis of *rosasite* corresponds with a kind of *zinc-malachite*, $(Cu, Zn)CO_3.(Cu, Zn)(OH)_2$. F. K. Biehl studied the aurichalcites of Tsumeb; those with a composition $3(Cu,Zn)CO_3.4(Cu,Zn)(OH)_2$ with $Cu : Zn = 2 : 1$ and sp. gr. 4·201, and $4(Cu,Zn)CO_3.5(Cu,Zn)(OH)_2$ with $Cu : Zn = 3 : 2$ and sp. gr. 4·137, are called *paraurichalcites;* while material with $(Cu,Zn)CO_3.(Cu,Zn)(OH)_2$ with $Cu : Zn = 9 : 2$ and sp. gr. 4·104 is called *cuprozincite.* E. W. Provost found a deposit on the brass binding screws of a Leclanché cell which had the composition of a *zinc copper amminochloride*, $Cu_2Zn_4Cl_6(NH_3)_4CO_3$, but there is nothing to show that this product is a chemical individual.

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§ 19. Zinc and Cadmium Nitrates

A soln. of **zinc nitrate** is obtained by dissolving the metal, the oxide, or hydroxide in nitric acid; and when the conc. soln. is allowed to crystallize, **hexahydrated zinc nitrate,** $Zn(NO_3)_2.6H_2O$, is obtained in "colourless, flattened, striated, four-sided prisms, with four-sided summits." This formula agrees with the analyses of T. Graham,[1] and N. A. E. Millon, but R. Schindler thought that $7H_2O$ best represented his analysis. Hydrates with $1\frac{1}{2}$, 2, 3, 4, $5\frac{1}{2}$, 6, and $9H_2O$ have not been reported, but the reports of several of these are based on insufficient evidence. The equilibrium conditions of the ennea-, hexa-, and tri-hydrates are illustrated in Fig. 50, which is based on the solubility determinations of F. Mylius and R. Funk between −29° and 36·4°; and of J. Ordway at higher temp. The percentage solubilities, *S*, are:

	−29°	−20°	−17°	0°	18°	36·4°	35°	40°	45·5°
S . . .	39·40	42·00	44·80	48·66	53·89	63·68	65·52	67·42	77·80 %
Solid phase .	$Zn(NO_3)_2.9H_2O$			$Zn(NO_3)_2.6H_2O$				$Zn(NO_3)_2.3H_2O$	

For the ice-line, R. Funk gave 35·03 per cent. at −16°, and F. Rüdorff, 18·43 per cent. at −7·4° and 11·19 per cent. at −3·6°. P. Dutoit and E. Grobet measured the temp. changes attending the progressive addition of sodium hydroxide to soln. of zinc nitrate and observed breaks corresponding with the formation of *zinc hydroxynitrate*, $Zn(OH)NO_3$, zinc hydroxide, and sodium zincate.

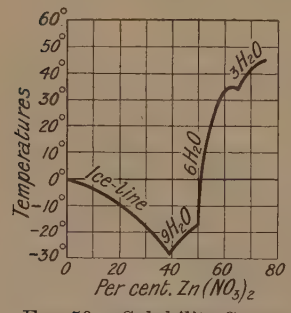

FIG. 50.—Solubility Curves of Zinc Nitrate.

A. Ditte made **hemitrihydrated zinc nitrate,** $Zn(NO_3)_2.1\frac{1}{2}H_2O$, by heating the hexahydrate until red vapours appear and dissolving the cold mass in monohydrated sulphuric acid. Much heat is thereby developed, and when the soln. cools, transparent, lustrous crystals appear. A. M. Wasilieff prepared what he regarded as **dihydrated zinc nitrate,** $Zn(NO_3)_2.2H_2O$, by cooling a soln. of zinc oxide in 97 per cent. nitric acid. H. C. Jones and H. P. Bassett found that **trihydrated zinc nitrate,** $Zn(NO_3)_2.3H_2O$, separates from the aq. soln. at 36° in needle-like crystals. R. Funk obtained the trihydrate by driving off two-thirds of the water from the hexahydrate, melting the product at 37° with more hexahydrate, rapidly cooling to 30°, and again heating to 34°. He also made it by keeping the hexahydrate at 37°–40° for many days, and by heating the hexahydrate with a little nitric acid on a water-bath and evaporating the soln. over sulphuric acid. The trihydrate is the stable solid phase in the presence of aq. soln. above 36°. A. M. Wasilieff claimed to have made rhomboidal crystals of **tetrahydrated zinc nitrate,** $Zn(NO_3)_2.4H_2O$, from a soln. of zinc oxide in nitric acid of sp. gr. 1·4. According to A. M. Wasilieff, the so-called **hemihenadeca-hydrated zinc nitrate,** $Zn(NO_3)_2.5\frac{1}{2}H_2O$, is a eutectic of

the hexa- and tetra-hydrates which freezes at 35·4°. H. C. Jones and H. P. Bassett made **enneahydrated zinc nitrate,** $Zn(NO_3)_2.9H_2O$, by cooling an aq. soln. of zinc nitrate to about −18°, R. Funk said −20°.

The crystallization of a conc. soln. of cadmium, or of cadmium oxide or hydroxide in nitric acid, furnishes crystals of **tetrahydrated cadmium nitrate,** $Cd(NO_3)_2.4H_2O$, "in prisms and needles, united," said F. Stromeyer, "in radiating masses." B. Franz studied the preparation of cadmium nitrate. The crystals are dissolved in hot water, and the soln. again crystallized. The preparation of highly purified cadmium nitrate has been discussed by W. S. Lorimer and E. F. Smith, and by E. A. Partridge. A. M. Wasilieff made the anhydrous salt by evaporating the water from the hydrate. Hydrates have been reported containing 2, 4, and 9 mols of water of crystallization. The range of stability of the two latter in aq. soln. is illustrated by the curve, Fig. 51. The percentage solubilities, S, are :

	−8·6°	−14·5°	−16°	−13°	0°	1°	30°	40°	59·5°
S . . .	25·5	35·9	36·3	37·3	52·3	52·6	58·4	61·4	56·6
Solid phase .	Ice			$Cd(NO_3)_2.9H_2O$			$Cd(NO_3)_2.4H_2O$		

The determinations from −4·2° to −8·6° are by F. Rüdorff, and the value at 59·5° is by J. Ordway ; the remainder are by R. Funk. A. M. Wasilieff traced the solubility curve of the anhydrous salt, and of the solid tetrahydrate, and found a break beyond the m.p. of the hydrate, 59·5°, descending to 44·5°, which is the eutectic temp. of the mixture, and corresponds with $Cd(NO_3)_2+2{\cdot}65H_2O$; the curve then rises continuously to the m.p. of the anhydrous salt.

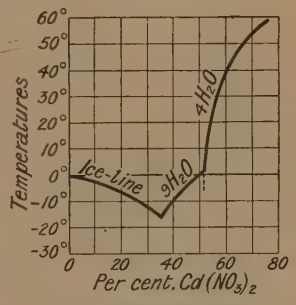

Fig. 51.—Solubility Curves of Cadmium Nitrate.

H. Lescœur prepared needle-like crystals of **dihydrated cadmium nitrate,** $Cd(NO_3)_2.2H_2O$, by adding conc. nitric acid to a soln. of the tetrahydrate. R. Funk also obtained it by keeping the tetrahydrate in a molten condition for some days, but found it difficult to isolate the crystals from the viscid mass. H. C. Jones and H. P. Bassett crystallized **enneahydrated cadmium nitrate,** $Cd(NO_3)_2.9H_2O$, from a supersaturated soln. of cadmium nitrate cooled to −16°. According to R. Funk, the crystals of the tetrahydrate in the soln. below 0° slowly pass into the higher hydrate. If the supersaturated soln. be cooled to −30°, crystals of the enneahydrate appear, the temp. rises to −16° and the cryohydrate is formed. A. M. Wasilieff could obtain neither the di- nor hexa-hydrates reported by R. Funk ; and he represented the low temp. crystals as the octohydrated salt. M. Hasselblatt measured the velocities of crystallization at 1 and 1000 kgrms. per sq. cm. press. and found a slight increase with rise of press.

F. W. Clarke [2] gave 2·065 for the **specific gravity** of hexahydrated zinc nitrate at 14°, and 2·455 for the sp. gr. of tetrahydrated cadmium nitrate at 17°. The sp. gr. of aq. soln. of zinc nitrate have been measured by A. C. Oudemanns, D. Dijken, J. Wagner, H. T. Barnes and A. P. Scott, H. C. Jones and F. H. Getman, F. Mylius and R. Funk, R. Dietz, etc. B. Franz found at 17·5°, for soln. with varying percentages of cadmium nitrate :

	1	5	10	15	25	30	35	45	50
Sp. gr. .	1·0099	1·0496	1·0968	1·1476	1·2640	1·3268	1·3906	1·5258	1·5984

G. Happart measured the contraction which occurs when zinc nitrate is dissolved in water. The sp. gr. of aq. soln. of cadmium nitrate has been measured by C. A. Valson, O. Grotrian, J. Wagner, F. J. Wershoven, R. de Muynck, M. le Blanc and P. Rohland, H. C. Jones and F. H. Getman, etc. B. Franz found at 15° for soln. with varying percentages of cadmium nitrate :

	5	10	15	20	25	35	45	5
Sp. gr. .	1·0528	1·0978	1·1516	1·2134	1·2842	1·4372	1·6471	1·7608

H. Sentis [3] found the **surface tension** of soln. of zinc nitrate containing n mols of salt in $100-n$ mols of water to be $2{\cdot}5n$. C. A. Valson observed the heights to which soln. of cadmium nitrate rise in capillary tubes. J. Wagner found the **viscosity** of aq. soln. of zinc and cadmium nitrates to be at 25° (water unity) :

	N-	$\frac{1}{2}N$-	$\frac{1}{4}N$-	$\frac{1}{8}N$-
$Zn(NO_3)_2$ . .	1·1642	1·0857	1·0390	1·0186
$Cd(NO_3)_2$ . .	1·1648	1·0742	1·0380	1·0117

J. C. Graham found the **diffusion** coeff. of 3 to 5 per cent. soln. of zinc nitrate to be $k=0{\cdot}640$. J. Thovert also measured this constant.

The **melting point** of anhydrous cadmium nitrate was found by A. M. Wasilieff [4] to be 350° ; that of the tetrahydrated cadmium nitrate, 59·5° ; and that of hexahydrated zinc nitrate was found by J. Ordway to be 36·4°. M. Hasselblatt found the m.p. of tetrahydrated cadmium nitrate was raised 7° when the press. was increased from 1 to 1000 kgrms. per sq. cm. W. A. Tilden gave 36·4° and J. L. R. Morgan and F. T. Owen, 44·07° ; J. Ordway gave 131° for the **boiling point** of the hexahydrate. A. Vogel and C. Reischauer found that the hexahydrate loses two-thirds of its water in vacuo over sulphuric acid ; T. Graham said half the water is lost. A. Vogel and C. Reischauer added that nitric acid is lost when the nitrate is warmed at 100° for a long time, and J. I. Pierre, that all the water is gradually lost when the nitrate is heated for a long time in a stream of air at 105°, while R. Schindler found that when the nitrate is heated above 100°, it loses nitric acid, nitrogen peroxide, and oxygen. A. Ditte said that the hemitrihydrate melts when heated, and gives off water and nitrous vapours. R. Funk found that trihydrated zinc nitrate melts at 45·5°, and on exposure to air, it is very soon converted into the hexahydrate. A. M. Wasilieff found the eutectic temp. of the tetra- and di-hydrates is 38·4°, and of the hexa- and tetra-hydrates, 35·4° ; he added that the m.p. of the tetrahydrate is 45·5°. N. A. Puschin found that the transition point of $Cd(NO_3)_2.4H_2O \rightarrow Cd(NO_3)_2$ occurs at 58·7° under atm. press., and at a press. p kgrms. per sq. cm., the transition temp., θ, is $\theta=58{\cdot}7+0{\cdot}00813p$.

According to K. von Hauer, and A. Hébert and G. Reynaud, tetrahydrated cadmium nitrate melts in its water of crystallization at 100°, at 59·5°, according to J. Ordway, R. Funk, and W. A. Tilden. J. Ordway gave 132° for the b.p. A. Hébert and G. Reynaud found the tetrahydrate, in vacuo, loses water and nitrous vapours, and the residue, according to H. Lescœur, contains insoluble cadmium oxide, and the soluble dihydrate. A. Ditte found a slight smell of nitrous fumes is given off by the molten salt. According to N. A. Puschin, the m.p. is 91° at 8000 kgrms. press., and when the press. exceeds 8000 kgrms., the m.p. is depressed. R. Funk gave 130° for the m.p. of dihydrated cadmium nitrate. J. L. R. Morgan and F. T. Owen found the **latent heat of fusion** of trihydrated zinc nitrate to be 34·3 cals. per grm., and N. A. Puschin obtained 26·3 Cals. per mol at atm. press. for tetrahydrated cadmium nitrate.

F. Rüdorff [5] measured the **lowering of the freezing point** of soln. of zinc and cadmium nitrates ; and H. C. Jones and F. H. Getman found for soln. containing M mols of zinc nitrate per litre :

M . .	0·065	0·129	0·258	0·516	1·290	1·548	1·806	2·064	2·580
$\delta\theta$ . .	0·322°	0·633°	1·281°	2·812°	8·930°	11·800°	14·720°	18·240°	27·000°
$\delta\theta/M$.	4·95	4·90	4·96	5·45	6·92	7·69	8·15	8·83	10·46

and similarly for soln. of cadmium nitrate :

M . .	0·0845	0·1691	0·3382	0·6764	1·0146	1·6910	2·7056
$\delta\theta$ . .	0·443	0·865	1·802	2·028	6·540	12·930	26·000
$\delta\theta/M$.	5·24	5·12	5·33	5·96	6·45	7·65	9·61

J. L. R. Morgan and F. T. Owen studied hydrated zinc nitrate as a solvent for the

f.p. method of determining mol. wt. and obtained 58·6 for the f.p. constant J. Schröder and H. Steiner found the **molecular weight** of zinc nitrate in methyl acetate as solvent, to be 100·7 to 189·1—calculated for $Zn(NO_3)_2$, 189·5. G. Tammann measured the **osmotic pressure** of soln. of zinc nitrate. G. Tammann measured the **lowering of the vapour pressure** of water at 100°, and found that with 9·31, 32·53, and 78·06 grms. of zinc nitrate per 100 grms. of water, the vap. press. was lowered 16·3 mm., 78·0 mm., and 231·5 mm. respectively; and with 8·18, 60·37, and 86·73 grms. of cadmium nitrate in 100 grms. of water, the vap. press. was lowered 10·7 mm., 102·2 mm., and 159·5 mm. respectively. H. Lescœur found the vap. press. of a sat. soln. of zinc nitrate at 20° to be 9·6 mm.; he also found the vap. press. of the trihydrate to be less than 2 mm. at 20°, and for the hexahydrate, 10 mm. at 20°. H. Lescœur gave 10 mm. for the dissociation press. of sat. soln. of cadmium nitrate at 20°, for $Cd(NO_3)_2.4H_2O$, 9·3 mm.; for $Cd(NO_3)_2.2\frac{1}{2}H_2O$, 8·4 mm.; and for $Cd(NO_3)_2.2{\cdot}1H_2O$, below 3 mm.

J. C. G. de Marignac [6] found the **specific heat** of soln. of zinc nitrate with $10H_2O$, $25H_2O$, $50H_2O$, and $200H_2O$ to be respectively 0·5906, 0·7176, 0·8234, and 0·9461 between 20° and 52°. M. Berthelot gave for the **heat of formation,** (Zn, N_2, $3O_2$, Aq.)=$Zn(NO_3)_{2aq.}$+131·7 Cals.; and J. Thomsen gave (Zn, O_2, N_2O_4, $6H_2O$) =140·82 Cals.; (Cd, N_2, $3O_2$, H_2O)=113·3 Cals.; and (Cd, N_2, $3O_2$, $4H_2O$ =121·16 Cals. For the **heat of dilution,** J. Thomsen gave for $Zn(NO_3)_2$+$10H_2O$ when diluted with

Mols H_2O	15	20	50	100	200
Cals.	0·914	1·148	1·203	1·111	1·071 Cals.

for a mol of $Zn(NO_3)_2.6H_2O$ with 400 mols of water, —5·84 Cals., for a mol of $Cd(NO_3)_2.H_2O$, 4.18 Cals., and for a mol of $Cd(NO_3)_2.4H_2O$, —5·04 Cals. For the **heat of neutralization** in very dil. soln., J. Thomsen gave for $Zn(OH)_2$+$2HNO_3$ =$2H_2O$+$Zn(NO_3)_2$+9·915 Cals., and M. Berthelot gave 9·8 Cals.; J. Thomsen also gave for $Cd(OH)_2$+$2HNO_3$=$2H_2O$+$Cd(NO_3)_2$+20·243 Cals. F. Braun found that but 77 per cent. of the heat of formation of cadmium nitrate can be converted into electrical energy.

H. C. Jones and F. H. Getman [7] measured the **index of refraction,** μ, for soln. containing M mol of zinc nitrate per litre:

M	0·065	0·129	0·258	0·516	1·132	1·548	2·064	2·580
μ	1·32766	1·32949	1·33272	1·34021	1·35374	1·36775	1·37981	1·39098

and for cadmium nitrate:

M	0·0845	0·1691	0·6746	1·0146	1·6910	2·3674	3·0438	3·3820
μ	1·32355	1·33070	1·34588	1·35580	1·36794	1·37379	1·40792	1·41534

Measurements of soln. of zinc nitrate were also made by D. Dijken, and of cadmium nitrate by M. le Blanc and P. Rohland, and by R. de Muynck. A. Hébert and G. Reynaud studied the specific absorption of **X-rays** by cadmium nitrate. A. E. Garrett found that above 360°, cadmium nitrate can ionize the surrounding air. W. N. Hartley has measured the absorption spectrum of soln. of zinc nitrate. J. R. Collins measured the **ultra-red absorption spectrum** of aq. soln. of the nitrate.

The **electrical conductivity** of soln. of zinc nitrate has been determined by S. Arrhenius,[8] H. C. Jones and co-workers, and C. Freund. H. C. Jones gave for soln. containing a mol of zinc nitrate in v litres the mol. conductivities μ:

v	4	8	52	128	512	1024	2048	4096
μ at 0°	80·6	87·6	100·0	110·4	114·1	117·1	120·4	124·4
μ at 65°	258·65	289·67	343·09	384·97	415·20	428·50	434·82	445·53

The temp. coeff. of the conductivity has been measured by H. C. Jones and co-workers. A. E. Garrett found that the conductivity of zinc nitrate is increased by raising the temp. O. Grotrian, E. Bouty, S. Labendzinsky, and F. J. Wershoven,

measured the electrical conductivity of soln. of cadmium nitrate. H. C. Jones and F. H. Getman found at 0° :

v	0·29	0·42	0·59	0·98	1·48	2·95	5·91	11·83
μ	10·60	27·30	38·43	57·10	64·6	81·0	92·6	99·7
α	5·30	13·6	19·2	28·6	32·3	40·5	46·3	49·9

where α denotes the values for the percentage **degree of ionization ;** for soln. of zinc nitrate the percentage degree of ionization is :

v	4	8	32	128	512	1024	2048	4096
α at 0°	64·8	70·4	80·4	88·7	91·9	94·1	96·8	100·0
α at 65°	58·1	65·0	77·0	86·4	93·2	96·2	97·6	100·0

R. Benz studied the conductivity of alcoholic soln. of cadmium nitrate. S. Labendzinsky also measured the degree of ionization of soln. of zinc and cadmium nitrates. The *temperature* coeff. of the conductivity has been measured by O. Grotrian, and F. J. Wershoven. B. Piesch measured the effect of *pressure* on the conductivity of soln. of zinc nitrate. C. L. Weber, and A. Chassy measured the **transport numbers** of the ions with soln. of zinc nitrate ; and G. Carrara with aq. and alcoholic soln. of cadmium nitrate. S. Labendzinsky measured the **potential** of zinc against N-$Zn(NO_3)_2$ and a calomel electrode. E. Bouty, and A. Ebeling measured the **thermoelectric force** of zinc against soln. of zinc nitrate ; and E. Bouty, and A. Hagenbach, of cadmium against soln. of cadmium nitrate.

Basic salts.—According to J. Walker and E. Aston,[9] the **hydrolysis** of a $\frac{1}{2}N$-soln. of zinc nitrate at 80° is 0·019 per cent., and of a $\frac{1}{2}N$-soln. of cadmium nitrate 0·014 per cent. A. Vogel and C. Reischauer found that a neutral soln. of zinc nitrate dissolves some zinc oxide ; and H. L. Wells obtained prismatic crystals of **trihydrated zinc monoxynitrate,** $Zn(NO_3)_2.ZnO.2H_2O$, in a similar manner. It furnishes different decomposition products when treated with alcohol or water. J. Ordway, and G. A. Bertels reported **trihydrated zinc monoxytrinitrate,** $3Zn(NO_3)_2.ZnO.3H_2O$; H. L. Wells, and G. A. Bertels reported **tetradecahydrated zinc trioxytetranitrate,** $4Zn(NO_3)_2.3ZnO.14H_2O$, among the products of the decomposition of the zinc monoxynitrate by water. A. Ditte prepared **hydrated zinc dioxynitrate,** $Zn(NO_3)_2.2ZnO.nH_2O$, by washing the yellow powder—$8ZnO.N_2O_5.4H_2O$—with water, until the runnings were free from zinc nitrate. The product decomposes when heated without melting ; it is soluble in nitric acid ; and it is not acted on by a soln. of zinc nitrate. G. A. Bertels and J. Ordway boiled the neutral zinc nitrate until it had lost 42 per cent. in weight, and found that the solidified glassy residue had the composition : $Zn(NO_3)_2.3ZnO.3H_2O$—**trihydrated zinc trioxynitrate.** C. F. Gerhardt prepared this salt in prismatic needles. By heating a soln. of two parts of zinc nitrate with one part of water in a sealed tube at 310° M. Athanasesco prepared white needles of the same composition : $Zn(NO_3)_2.3ZnO.3H_2O$, or, as he puts it, $HO.NO : (OZnOH)_2$. The crystals lose their water at 180° ; they are insoluble in water and soluble in dil. acids. M. Athanasesco also prepared the *tetrahydrate* in white needles by boiling a very conc. neutral soln. of zinc nitrate (1 : 1) with zinc. They lose their water of crystallization at 130°, and decompose when heated above 180°. R. Schindler also prepared a white powder which he regarded as a *dihydrate* by digesting the yellow powder, $8ZnO.N_2O_5.4H_2O$, with a neutral soln. of zinc nitrate.

A. Terreil prepared what he regarded as **pentahydrated zinc tetroxynitrate,** $Zn(NO_3)_2.4ZnO.5H_2O$, by the action of an excess of zinc on a boiling soln. of zinc nitrate, and cooling the syrupy mass obtained by evaporation. The undecomposed nitrate was removed by washing with water. The fine acicular crystals are insoluble in cold water, and decompose when heated. G. Rousseau and G. Tite obtained the *hexahydrate* by heating in a sealed tube at 100°, the hydrated normal salt mixed with marble. The needle-like crystals are slowly decomposed by cold, and rapidly by boiling water. J. Habermann obtained what he regards as a *hemihenadeca hydrate,* $Zn(NO_3)_2.4ZnO.5\frac{1}{2}H_2O$, by the action of dil. ammonia on a neutral soln. of

zinc nitrate. The crystals were insoluble in cold water. M. Berthelot has also studied this basic salt. A. Vogel and C. Reischauer prepared fine crystals of what they regarded as **zinc heptoxydinitrate,** $9ZnO.2N_2O_5$, or $2Zn(NO_3)_2.7ZnO$, by warming the neutral salt for a long time at 100°. J. Ordway and G. A. Bertels prepared **trihydrated zinc pentoxynitrate,** $Zn(NO_3)_2.5ZnO.3H_2O$, by the action of water on trihydrated zinc monoxynitrate. J. Ribau also obtained what he regarded as a *heptahydrate* and an *octohydrate* by the action of an excess of zinc on a boiling soln. of zinc nitrate. According to P. Grouvelle, **tetrahydrated zinc heptoxynitrate,** $8ZnO.N_2O_5.4H_2O$, or $Zn(NO_3)_2.7ZnO.4H_2O$, is produced by adding insufficient ammonia required for the complete precipitation of zinc nitrate. According to R. Schindler, the precipitate retains some ammonia. When the normal salt is heated until it has become nearly solid, P. Grouvelle found the product corresponded with the *dihydrate* of zinc heptoxynitrate. R. Schindler also said that if the molten nitrate be heated until it becomes opaque, and then washed with water, the yellow powder which remains has the same composition.

H. C. Klinger obtained iridescent rhombic plates of **trihydrated cadmium monoxynitrate,** $Cd(NO_3)_2.CdO.3H_2O$, by adding lead hydroxide to a hot soln. of cadmium nitrate ; by heating cadmium nitrate ; and by dissolving cadmium hydroxide in a soln. of the nitrate. The product was washed with alcohol and dried in a desiccator. H. L. Wells obtained prismatic crystals from a sat. soln. of cadmium oxide in a conc. soln. of the nitrate. The product loses a mol of water between 120° and 130° ; it is decomposed by water and alcohol. The latter acts more rapidly than water, and the final product is the hydroxide. A. Ditte also obtained this compound. According to H. L. Wells, H. C. Klinger's analyses agree with $4Cd(NO_3)_2.3CdO.7H_2O$. G. Rousseau and G. Tite reported the formation of lamellar crystals of **octohydrated cadmium trioxydinitrate,** $2Cd(NO_3)_2.3CdO.8H_2O$, by heating the normal nitrate with marble in a sealed tube, between 300° and 350°, and washing with boiling alcohol. The product is immediately decomposed by water to amorphous cadmium henadecaoxynitrate, $Cd(NO_3)_2.11CdO.11H_2O$, by adding very dil. aq. ammonia to a boiling conc. soln. of normal cadmium nitrate. The product is but sparingly soluble in water.

Zinc nitrate deliquesces in air ; K. von Hauer, and W. Meissner [10] noted that tetrahydrated cadmium nitrate deliquesces in air. Both zinc and cadmium nitrates are readily soluble in **water.** J. G. Children noted that tetrahydrated cadmium nitrate is soluble in **ethyl alcohol** but does not impart any peculiar colour to the flame. G. Carrara and L. d'Agostini found that cadmium nitrate is soluble in **methyl alcohol ;** P. Dutoit, and R. Benz, in **acetone ;** A. Naumann in **ethyl acetate ;** and L. Kahlenberg, in **pyridine.** H. Demarçay found that **lead hydroxide** precipitates the zinc as basic nitrate completely from a soln. of the salt. A. Mailhe studied the action of **cupric hydroxide** on an aq. soln. of zinc nitrate and noted the formation of a basic salt, $Zn(NO_3)_2.3CuO.3H_2O$. A. Mailhe found that with cadmium nitrate, **mercuric oxide** gives a white precipitate of the basic salt, $CdO.Hg(NO_3)_2.3H_2O$. M. C. de Schuyten found that **chlorine, bromine,** or **iodine** forms the zinc halide with aq. soln. of zinc nitrate. H. Demarçay found that zinc nitrate detonates when sprinkled on hot **carbon,** and gives a reddish flame. L. P. Perman found a reaction between **arsenious oxide** and cadmium nitrate. According to A. Ditte, hemitrihydrated zinc nitrate is readily soluble in **nitric acid**—100 parts of water at 13° dissolve 28 parts of the salt, and at 55°, 55 parts of the salt. K. Drücker found that when aq. **ammonia** is added to a soln. of zinc nitrate, an amorphous white precipitate of the basic salt is produced. E. C. Franklin and C. A. Kraus found that the soln. of zinc nitrate in aq. ammonia at once gives a precipitate with ammonium chloride, with ammonium bromide the precipitate is formed more slowly, and none with ammonium iodide ; ammonium sulphide gives a white precipitate ; ammonium chromate a flocculent precipitate ; and ammonium borate, a white precipitate. F. M. G. Johnson and N. T. M. Wilsmore found cadmium nitrate is soluble in liquid ammonia. W. Herz studied the equilibrium

conditions in the reaction between **ammonium nitrate** and cadmium hydroxide: $Cd(NO_3)_2+2NH_4OH \rightleftharpoons Cd(OH)_2+2NH_4NO_3$. A. Eckstädt studied the catalytic effect of cadmium nitrate on the reaction between nitric acid and iodine.

G. André prepared deliquescent crystals of **zinc tetrammino-nitrate.** $[Zn(NO_3)_2(NH_3)_4]_3.2H_2O$, by passing ammonia through a soln. of zinc nitrate, and evaporating so as to avoid a rise of temp. F. Ephraim gave 206° for the decomposition temp. of zinc tetrammino-nitrate, and he found that the crystalline tetrammine changed into **zinc hexammino-nitrate,** $[Zn(NH_3)_6](NO_3)_2$, when treated with ammonia at 0°. The latter decomposed at 31·5°. M. I. Konowaloff measured the electrical conductivity of soln. of zinc tetrammino-nitrate, and likewise of soln. of **cadmium hexammino-nitrate,** $Cd(NO_3)_2.6NH_3$. The anhydrous cadmium salt was prepared by G. André by saturating an ammoniacal soln. of cadmium nitrate with ammonia; the soln. gives a white precipitate when treated with cold water. Crystals of the monohydrate were also prepared by dissolving an excess of cadmium nitrate in 20 per cent. aq. ammonia. The voluminous precipitate dissolves when the mixture is alternately warmed and cooled. The salt blackens when heated and decomposes with a slight explosion. F. M. G. Johnson and N. T. M. Wilsmore measured the e.m.f. of conc. cells of tetrahydrated cadmium nitrate in liquid ammonia at −33·5°. G. André prepared a **basic zinc tetrammino-nitrate,** $3Zn(NO_3)_2.10ZnO.4NH_3.18H_2O$, by the action of precipitated zinc oxide on a warm aq. soln. of ammonium nitrate. The salt is insoluble in cold water, and decomposed by warm water into zinc oxide, etc. H. Morin reported the formation of **ammonium cadmium nitrate,** by the action of a rod of cadmium on a soln. of ammonium nitrate.

M. Hasselblatt studied the fusion curves of isomorphous mixtures of tetrahydrated **cadmium and calcium nitrates.** The stable form of calcium nitrate furnishes a eutectic at 40·6° when 91 per cent. of $Cd(NO_3)_2.4H_2O$ is present. The unstable form gives a continuous series of mixed crystals with the cadmium salt. The effect of increased press. up to 3000 kilos. per sq. cm. on the system has now been investigated. The general form of the diagram is unchanged. The press. temp. curve for mixed crystals containing a high proportion of the calcium salt could not be followed at higher press. on account of the rapid change of the calcium salt into the stable form. Excess of the cadmium salt inhibits this change, but as the press. increases, more cadmium salt is needed to produce this effect. With increasing press., the m.p. of the stable calcium salt rises much more rapidly than that of the unstable. The latter does not form mixed crystals with cadmium nitrate. The lowering of the m.p. of the stable calcium salt by the cadmium salt is independent of the press. With increasing press., the eutectic point moves towards the cadmium side; at 1000 kgrms. per sq. cm. it is at 79 per cent. calcium nitrate, 47·8°; at 2000 krgms. per sq. cm. 74 per cent. and 55°; and at 3000 kgrms. per sq. cm. 71 per cent. calcium nitrate and 61·5°.

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§ 20. Zinc and Cadmium Phosphates

The mineral *hopeite* found in the calamine mines of Altenburg (Aix-la-Chapelle) was named by D. Brewster [1] after T. C. Hope of Edinburgh; A. Breithaupt called it prismatoidal *zincphyllite*. N. Nordenskiöld showed that it is probably a hydrated zinc phosphate with a little cadmium phosphate. A. des Cloizeaux, and C. Friedel and E. Sarasin showed that hopeite is essentially zinc orthophosphate, $Zn_3(PO_4)_2.4H_2O$. A. Schrauf showed that hopeite is closely related to eggonite. L. J. Spencer showed that the mineral is dimorphous, and exists in rhombic and triclinic forms: the former is called hopeite, and the latter parahopeite; hopeite also occurs in two modifications—α-hopeite and β-hopeite—distinguished by their optical properties, and their dehydration curves. All three varieties are found at Brocken Hill (N.-W. Rhodesia).

E. Mitscherlich found that normal **zinc orthophosphate,** $Zn_3(PO_4)_2$, is precipitated on mixing a soln. of a zinc salt with ammonium, potassium, or sodium hydrophosphate, and he noted that the supernatant liquid becomes acidic. R. Schindler, and H. Debray found that when dil. soln. of zinc sulphate and sodium hydrophosphate are mixed in the cold, a translucent jelly is first produced, and this soon becomes opaque, and aggregates into a fine white crystalline powder; if the soln. are mixed boiling hot, no jelly is produced, but the pulverulent precipitate is produced at once. W. Heintz also obtained the same product by working with acetic acid soln. According to W. Heintz, and H. Debray, the same compound is also produced when zinc carbonate is digested with an aq. soln. of phosphoric acid, not in excess. A. de Schulten obtained artificial crystals of hopeite by mixing a soln. of 4·5 grms. of heptahydrated zinc sulphate in 2 litres of cold water with a soln. of dodecahydrated sodium hydrophosphate in a litre of cold water. According to A. de Schulten, the composition corresponds with $Zn_3(PO_4)_2.8H_2O$; C. Friedel and E. Sarasin gave $Zn_3(PO_4)_2.4H_2O$; R. Schindler, and T. Graham, $Zn_3(PO_4)_2.2H_2O$; W. Skey, $Zn_3(PO_4)_2.5H_2O$; and A. Reynoso, $Zn_3(PO_4)_2.6H_2O$. L. J. Spencer's analyses of both hopeite and parahopeite correspond with $Zn_3(PO_4)_2.4H_2O$. G. Cesaro believed that the formula $5Zn_3(PO_4)_2.4Zn(PO_3)_2.7Zn(OH)_2.21H_2O$ best represents L. J. Spencer's analyses, but allowing for the impurities present in the native samples, the formula $Zn_3(PO_4)_2.4H_2O$ best represents the composition of hopeite and parahopeite. N. E. Eberly, C. V. Gross, and W. S. Crowell studied the ternary system ZnO—P_2O_5—H_2O at 25° and 37° as far as 55 per cent. P_2O_5. Their results are summarized in Fig. 52, where the dotted line refers to 37° and the other lines to 25°. The first branch of the curve represents the solubility of tetrahydrated zinc orthophosphate, $Zn_3(PO_4)_2.4H_2O$, in phosphoric acid, and the position for the curve 37° shows that the solubility decreases as the temp. rises. At *A* (25°) or *A'* (37°) there is a quadruple point where the tetrahydrated normal salt is in equilibrium with trihydrated hydrophosphate, $ZnHPO_4.3H_2O$; there is another quadruple point at *B* (25°), where the latter phase is in equilibrium with the dihydrated dihydrophosphate, $Zn(H_2PO_4)_2.2H_2O$. The monohydrated hydrophosphate, $ZnHPO_4.H_2O$, appears at 37° but not at 25°; and the quadruple points *B*

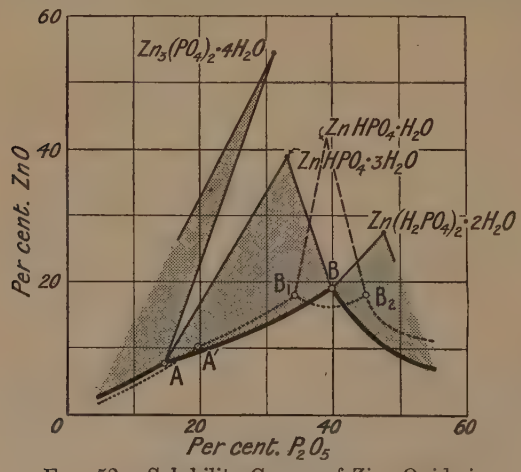

Fig. 52.—Solubility Curves of Zinc Oxide in Phosphoric Acid.

and B_2 represent this phase in equilibrium respectively with the trihydrated hydrophosphate and the dihydrated dihydrophosphate.

A. de Schulten prepared anhydrous zinc orthophosphate by melting together a mixture of the hydrated salt with zinc chloride, or by heating in a sealed tube at 250°, a mixture of hydrated zinc orthophosphate with a conc. soln. of zinc chloride. F. Stromeyer made **cadmium orthophosphate** by adding to a soln. of a cadmium salt sodium hydrophosphate, A. de Schulten used normal sodium phosphate; and A. Reynoso prepared the orthophosphate by heating the pyrophosphate with water in a sealed tube at 280°–300° for 5–6 hrs.

According to A. de Schulten, the **crystals** of anhydrous zinc orthophosphate are rhombic prisms. Hopeite was found by L. J. Spencer to occur usually in aggregates of acicular crystals, or in lamellæ. The crystals are rhombic bipyramids with axial ratios $a:b:c=0{\cdot}5786:1:0{\cdot}4753$, and A. de Schulten found the axial ratios with the artificial crystals to be $a:b:c=0{\cdot}5759:1:0{\cdot}4759$. L. J. Spencer stated that the imperfect crystals of parahopeite which were available are probably triclinic. N. E. Eberly and co-workers described the crystals of the tetrahydrate as "shining rhombic plates." The **specific gravity** of anhydrous zinc phosphate was found by A. de Schulten to be 3·998 at 15°; and L. J. Spencer gave 3·04 for the sp. gr. of α-hopeite, 3·03 for β-hopeite; J. D. Dana gave 2·76–2·85 for hopeite; and A. de Schulten gave 3·109 for the artificial crystals. The **hardness** of hopeite is between 2·5 and 3·25 on Mohs' scale; that of parahopeite is 3·75.

A. de Schulten found that zinc orthophosphate melts at a bright red heat; and F. Stromeyer found cadmium orthophosphate melts to a colourless glass at a white heat. When α-hopeite is heated to 105°, it becomes opaque, while β-hopeite becomes opaque at 140°; and parahopeite becomes white at 163°. The percentage loss of water at different temp. was found by L. J. Spencer to be:

	114°	135°	163°	180°	203°	233°	240°	290°
α-hopeite . .	5·2	8·5	—	9·8	10·1	—	14·9	15·8
β-hopeite . .	2·5	7·9	—	11·1	11·7	—	13·3	15·8
Parahopeite . .	—	—	1·9	—	11·6	15·5	—	—

Curves are plotted from these results in Fig. 53. According to L. J. Spencer, the **double refraction** of both varieties of hopeite is negative, that of parahopeite is positive; the axial angle of α-hopeite is 58·5°, and that of β-hopeite, 32·5°. The mean **index of refraction** of hopeite is 1·60, that of parahopeite is 1·62. A. des Cloizeaux gives for the index of refraction $\mu_\beta=1{\cdot}471$ for Na-light, and 1·469 for red light; G. Cesaro gave 1·6 for Na-light, and he found $\gamma-\alpha=0{\cdot}0115$; $\gamma-\beta=0{\cdot}0022$; and $\beta-\alpha=0{\cdot}0093$. E. Goldstein studied the **cathodo-phosphorescence** of cadmium phosphate; and E. L. Nichols, the brightness of the luminescence of the same salt.

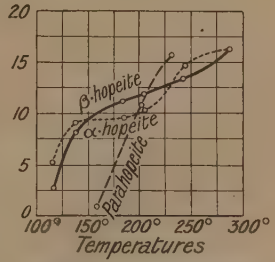

FIG. 53.—Dehydration Curves of Hopeite and Parahopeite.

Anhydrous zinc orthophosphate was found by A. de Schulten to be but slowly soluble in dil. acetic acid; and the hydrated phosphate was found by R. Schindler to be "insoluble" in water, easily soluble in dil. acids, and soluble in aq. ammonia, ammonium carbonate, sulphate, or nitrate; according to G. C. Stone, the solubility of zinc orthophosphate in an ammoniacal soln. of ammonium chloride distinguishes it from the corresponding salts of cadmium and magnesium. Zinc orthophosphate was found by W. Skey to give crystalline compounds with the corresponding phosphates of cobalt and nickel. F. Stromeyer also stated that cadmium orthophosphate is "insoluble" in water. C. Immerwahr measured the very sparing solubilities of zinc and cadmium phosphates in water. A. Colson found that the speed of decomposition of zinc orthophosphate by hydrogen sulphide, at a constant temp., is proportional to the square of the press. of the

gas, but at low press. the absorption is rather slower. The speed of the reaction is twice as fast at 160° as at 100°.

L. J. Spencer reported that crystals of the basic zinc orthophosphate, $4ZnO.P_2O_5.H_2O$, or $Zn_3(PO_4)_2.Zn(OH)_2$, or $Zn_2(OH)PO_4$, occurs as a mineral, *tarbuttite*, at Brocken Hill (N.-W. Rhodesia). The crystals are triclinic pinacoids, with the axial ratios $a:b:c=0{\cdot}9583:1:1{\cdot}3204$, and $\alpha=102°\ 37'$, $\beta=123°\ 52'$, and $\gamma=87°\ 25'$. Tarbuttite has a composition analogous with *adamite*, the corresponding arsenate, but the two minerals are not isomorphous. The crystals have a strong negative double refraction; and the indices of refraction are 1·704 and 1·668. The sp. gr. of the colourless crystals is 4·15, and of the yellow crystals 4·12; and the hardness is 3·75. T. L. Walker and A. L. Parsons reported *spencerite*, $Zn_3(PO_4)_2.Zn(OH)_2.3H_2O$.

C. F. Wenzel dissolved zinc carbonate or phosphate or the metal in an excess of phosphoric acid, and on evaporation, obtained a gum-like mass which readily fused to a transparent glass. If a little alkali be added to the aq. soln., normal zinc phosphate is deposited. T. Graham prepared lamellar crystals of **monohydrated zinc hydrophosphate,** $ZnHPO_4.H_2O$, by mixing soln. of 3 parts of zinc sulphate and of 4 parts of sodium hydrophosphate. Each dissolved in 32 parts of hot water. The zinc sulphate is here in excess; if the sodium hydrophosphate be in excess normal zinc phosphate is produced. The crystals do not lose water at 100°, but below 230°, they give off two-thirds of their combined water; and at a red heat, they fuse and lose all their water. W. Heintz could not confirm T. Graham's results. The conditions of equilibrium of the monohydrate at 37°, and of the trihydrate are illustrated by the curves of Fig. 52. N. E. Eberly, C. V. Gross, and W. S. Crowell found that the monohydrate forms small, hard, transparent needles with an extinction oblique to the long axis, and which are probably triclinic; while the trihydrate forms "sticky, thread-like crystals agglomerating into masses like cotton-wool. The optical properties could not be observed." When zinc dihydrophosphate is treated with water, W. Demel found that a white insoluble crystalline powder, $10ZnO.4P_2O_5.10H_2O$, or possibly $2Zn_3(PO_4)_2.4ZnHPO_4.8H_2O$, is formed which loses 1·6 per cent. of water at 100° and 10·03 per cent. at 280°.

According to A. de Schulten, the acid phosphate $5CdO.2P_2O_5.5H_2O$, or $Cd_3(PO_4)_2.2CdHPO_4.4H_2O$, is precipitated when a soln. of a cadmium salt is treated with ordinary sodium phosphate; the precipitate, at first amorphous, soon becomes crystalline. Good crystals were made by dissolving cadmium carbonate in 250 c.c. of phosphoric acid of sp. gr. 1·10, aided by heat, until a slight precipitate of cadmium phosphate is produced. The mixture is heated on a water-bath and slowly mixed with 500 c.c. of 3 per cent. aq. ammonia. The same compound is formed by heating cadmium dihydrophosphate to 100°. The prismatic crystals belong to the monoclinic system, and have the axial ratios $a:b:c=1{\cdot}8965:1:0{\cdot}5159$, and they are isomorphous with the corresponding manganese salt, the mineral *hureaulite*. The sp. gr. of the crystals ranges from 3·96–4·15; the double refraction is negative. The crystals lose their water at a red heat, and fuse at a white heat—the residue has the composition $5CdO.2P_2O_5$. According to A. de Schulten, by fusing cadmium chloride or bromide with normal cadmium phosphate, or the phosphate $Cd_3(PO_4)_2.2CdHPO_4.4H_2O$, and washing the product with water, prismatic or pyramidal crystals of **cadmium chloroapatite,** $3Cd_3(PO_4)_2.CdCl_2$, of sp. gr. 5·46 at 15°, or **cadmium bromoapatite,** $3Cd_3(PO_4)_2.CdBr_2$, remain undissolved.

W. Demel prepared **dihydrated zinc dihydrophosphate,** $Zn(H_2PO_4)_2.2H_2O$, by dissolving zinc oxide in an excess of aq. phosphoric acid, 100 grms. of the acid dissolve 10 grms. of the oxide. The soln. on standing deposits triclinic crystals with axial ratios $a:b:c=1{\cdot}6002:1:1{\cdot}1393$. The diagram, Fig. 51, shows the conditions of equilibrium of this salt. The crystals are permanent in air, and lose up to 1·86 per cent. of water at 100°, and at the same time fuse at the edges. The compound is decomposed by water as indicated above. The crystals are stable in the presence of alcohol or ether; and dissolve in hydrochloric acid. A. de

Schulten evaporated at ordinary temp. a dil. soln. of phosphoric acid, sat. with $Cd_3(PO_4)_2.2CdHPO_4.4H_2O$, and obtained rhombic prisms of **dihydrated cadmium dihydrophosphate,** $Cd(H_2PO_4)_2.2H_2O$. The crystals have a sp. gr. of 2·741 at 15° ; they lose their water of crystallization at 100° ; and they are decomposed by water re-forming $Cd_3(PO_4)_2.2CdHPO_4.4H_2O$.

When a hot soln. of zinc sulphate is mixed with an excess of ammonium phosphate, H. Debray showed that amorphous **ammonium zinc phosphate,** $ZnNH_4PO_4$, is precipitated, and if kept in contact with the heated mother liquid for 10–15 mins., crystallization occurs. Advantage is taken of this in H. Tamm's process [2] for the gravimetric determination of zinc ; the washed precipitate is ignited in an oxidizing atm., and the metal weighed as zinc pyrophosphate, $Zn_2P_2O_7$. The **monohydrated ammonium zinc phosphate,** $ZnNH_4PO_4.H_2O$, was obtained by A. Bette [3] by adding ammonium phosphate, mixed with an excess of aq. ammonia, to a soln. of zinc sulphate, and digesting the mixture at ordinary temp. until the precipitate is crystalline, and the excess of ammonia has evaporated. The precipitate is washed, pressed between folds of filter paper, and dried. W. Heintz modified the procedure a little. If sodium phosphate is used instead of the ammonium salt, A. Bette found the washing of the precipitate is difficult. W. Heintz stated that the microscopic crystals are colourless rectangular plates ; and A. Bette added that they are insoluble in water, but soluble in soln. of ammonia, and potassium or sodium hydroxide. H. Debray stated that by the spontaneous evaporation of an acidified soln. of zinc chloride and ammonium phosphate, insoluble crystals of **monohydrated ammonium zinc dihydrophosphate,** $Zn(NH_4)HPO_4(H_2PO_4).H_2O$, are produced. H. Schweikert found that microscopic scales of a basic ammonium zinc phosphate, $6ZnO.8NH_3.3P_2O_5.4H_2O$, are produced when ammoniacal soln. of zinc sulphate and phosphoric acid are mixed and allowed to stand for some days. W. Heintz found the crystals of the same salt separate when the mixed soln. is exposed to the cold of a winter's day.

E. H. Miller and R. W. Page prepared monohydrated **ammonium cadmium phosphate,** $CdNH_4PO_4.H_2O$, by mixing a soln. of a cadmium salt with an aq. soln. of ammonium phosphate, and allowing the flocculent precipitate to stand until it becomes crystalline. S. Drewsen believes that $1\frac{1}{4}$ mols of water of crystallization are present. The salt is readily soluble in aq. ammonia and in acids ; and when boiled with water, the salt loses water and ammonia and forms normal cadmium phosphate. The monohydrate can be dried at 100°–103° without decomposition. E. H. Miller, M. Austin, and A. Carnot and P. M. Proromant recommend the process for the gravimetric determination of cadmium ; the washed precipitate can be ignited to cadmium pyrophosphate, $Cd_2P_2O_7$, and weighed.

H. Grandeau, and L. Ouvrard dissolved zinc or cadmium oxide, or a salt of these metals in fused alkali pyro- or ortho-phosphate, with or without an alkali chloride, and, after slowly cooling the fused mass, and extracting the soluble salts with water, obtained as a residue **sodium zinc phospate,** $ZnNaPO_4$, of sp. gr. 3·3 at 20° ; similarly also with **potassium zinc phosphate,** $ZnKPO_4$; **sodium cadmium phosphate,** $CdNaPO_4$, of sp. gr. 4·1 at 20° ; and **potassium cadmium phosphate,** $CdKPO_4$, of sp. gr. 3·8 at 20°. The rhombic crystals are sparingly soluble in water and acetic acid, but are readily dissolved by dil. mineral acids. P. Glühmann also prepared sodium cadmium phosphate. L. Ouvrard also prepared cubic crystals of **disodium zinc phosphate,** $Zn(Na_2PO_4)_2$, of sp. gr. 2·8 at 20° ; and **disodium cadmium phosphate,** $Cd(Na_2PO_4)_2$, by dissolving zinc or cadmium oxide in an excess of sodium pyrophosphate.

F. Stromeyer [4] prepared gelatinous **zinc pyrophosphate,** $Zn_2P_2O_7$, by precipitation from a zinc salt soln. with sodium pyrophosphate. The gelatinous precipitate shrinks considerably on drying, and A. Schwarzenberg found that if it be suspended in water, and sulphur dioxide passed through the liquid, the whole dissolves, and the soln., when boiled, deposits the salt as a crystalline powder. J. Müller made zinc pyrophosphate by treating insoluble potassium metaphosphate

with a sat. soln. of zinc sulphate at 70° for 4 days ; and by the prolonged action of a soln. of zinc sulphate on zinc triphosphate. As indicated above, zinc or cadmium pyrophosphate is obtained by calcining ammonium zinc or cadmium pyrophosphate. A. Schwarzenberg obtained **cadmium pyrophosphate,** $Cd_2P_2O_7$, by the action of a soln. of sodium pyrophosphate on a soln. of a cadmium salt, and crystalline plates may be obtained by the sulphur dioxide treatment employed for the zinc salt. A. de Schulten obtained it by fusing normal cadmium phosphate with cadmium bromide.

According to A. Schwarzenberg, the crystalline salt at 100° retains the eq. of 1½ mols of water, and, according to C. N. Pahl, 5 mols. Crystalline cadmium pyrophosphate at 100° retains the eq. of 2 mols of water ; F. W. Clarke gave 3·7556 for the sp. gr. of the zinc salt at 23° ; and A. de Schulten, 4·965 at 15° for the cadmium salt. According to P. Glühmann, cadmium pyrophosphate sinters without melting when heated to redness ; and, according to A. Carnot and P. M. Proromant, the salt is not volatile at a red heat, but melts at a bright red heat. A. Schwarzenberg found that both the amorphous and crystalline zinc or cadmium pyrophosphates are soluble in acids, in potassium hydroxide lye, and in aq. ammonia. Alcohol precipitates a syrupy mass from the ammoniacal soln. G. von Knorre found zinc pyrophosphate is insoluble in acetic acid. J. H. Gladstone found that zinc or cadmium pyrophosphate dissolves in an excess of a soln. of sodium pyrophosphate ; and F. Stromeyer, that when boiled with a soln. of sodium hydrophosphate, zinc pyrophosphate forms zinc dihydrophosphate and sodium pyrophosphate. P. Glühmann found calcined cadmium pyrophosphate is almost insoluble in acids, and is very sparingly soluble in cold water, but more soluble in hot water. According to A. Reynoso, when heated with water in a sealed tube at 280°–300° for 5–6 hrs., it decomposes into a soln. of an acid phosphate, and crystals of the normal phosphate. Similar results were obtained with cadmium pyrophosphate. According to A. Schwarzenberg, when zinc or cadmium pyrophosphate is calcined in a stream of hydrogen, a sublimate of metal and phosphoric acid is formed, some phosphine is produced, and a white mixture of phosphoric acid and metal remains.

A. Bette obtained **zinc ammino-pyrophosphate,** $3Zn_2P_2O_7.4NH_3.9H_2O$, by mixing a soln. of zinc chloride with enough ammonium chloride to prevent precipitation by ammonia, and then adding aq. ammonia, and a soln. of sodium pyrophosphate. The flocculent precipitate is washed until the runnings no longer give a turbidity with a soln. of silver nitrate, pressed between filter paper, and dried. According to C. N. Pahl, the solubility of zinc pyrophosphate in a soln. of sodium pyrophosphate appears to be greatest at 60° or 70°. K. A. Wallroth made **sodium zinc pyrophosphate,** $ZnNa_2P_2O_7$, and **sodium cadmium pyrophosphate,** $CdNa_2P_2O_7$, in white crystals by fusing the respective oxides in microcosmic salt at a bright red heat. The cold mass is leached with water and then with dil. hydrochloric acid. A. Wiesler made crystals of sodium zinc pyrophosphate by the action of zinc acetate on sodium trimetaphosphate. The crystals swell at a dull red heat, and fuse to a glass at bright redness. G. von Knorre obtained similar results. C. N. Pahl reported that hydrated $ZnNa_2P_2O_7$ could be obtained with 2½ mols of water by adding water to the syrupy liquid obtained by the spontaneous evaporation of a soln. of zinc pyrophosphate in one of sodium pyrophosphate ; with 3 and 3½ mols of water of hydration by evaporating the soln. respectively at 50° and 60° ; the latter also as a crystalline powder by adding alcohol to the soln. The salt with 8 mols of water was obtained in prismatic crystals by evaporation at 30°. He also prepared long prismatic crystals of $3Na_4P_2O_7.Zn_2P_2O_7.24H_2O$ from the syrupy liquid obtained by the spontaneous evaporation of an aq. soln. of zinc and sodium pyrophosphates. C. N. Pahl also obtained small prisms of $Na_4P_2O_7.4Zn_2P_2O_7.12H_2O$ from a soln. of zinc pyrophosphate in one of sodium pyrophosphate prepared at 60°–70° ; and if prepared at 70°–80°, $4Na_4P_2O_7.5Zn_2P_2O_7.20H_2O$. C. N. Pahl prepared $Na_2CdP_2O_7$ by adding cadmium chloride to a soln. of sodium pyrophosphate until the precipitate is no longer dissolved. The evaporation of the filtered soln. furnishes

prismatic crystals which melt at a red heat, and are insoluble in water. L. Ouvrard prepared **potassium zinc pyrophosphate,** $K_2ZnP_2O_7$, by melting together zinc oxide and potassium metaphosphate, or zinc phosphate and potassium chloride, and leaching out the soluble matter with water from the cooled salt. The crystals melt when heated, and they readily dissolve in acids. C. N. Pahl reported the formation of imperfect crystals of $4K_4P_2O_7.5Cd_2P_2O_7.20H_2O$ by a process similar to that employed for the corresponding sodium compound. L. Ouvrard prepared **potassium cadmium pyrophosphate,** $CdK_2P_2O_7$, in a similar manner.

J. J. Berzelius [5] prepared glassy zinc metaphosphate by burning zinc sulphophosphide, ZnP_3S_2. The product is soluble in water, and is sometimes regarded as **zinc dimetaphosphate,** ZnP_2O_6, which A. Glatzel made by the action of potassium dimetaphosphate on a soln. of zinc chloride; B. Reinitzer and H. Goldschmidt by the action of zinc on phosphoryl chloride: $9Zn+4POCl_3=6ZnCl_2+3ZnO+P_4O$, and $4ZnO+2POCl_3=ZnP_2O_6+3ZnCl_2$, which proceeds slowly at ordinary temp., or more rapidly at 100°; and T. Fleitmann by evaporating zinc oxide, or a zinc salt of a volatile acid, with an excess of phosphoric acid, and heating the product to 350°. T. Fleitmann also made crystals of the *tetrahydrate*, $ZnP_2O_6.4H_2O$, by mixing a soln. of ammonium dimetaphosphate with an excess of zinc chloride. The compound melts to a clear glass at a strong red heat, and it is decomposed by boiling with sulphuric acid. J. F. Persoz, and T. Fleitmann made what may have been **cadmium dimetaphosphate,** CdP_2O_6, by mixing cadmium nitrate first with metaphosphoric acid, and then with aq. ammonia in which menstruum the precipitate dissolves, but separates again when the soln. is exposed to air. A. Glatzel obtained a white crystalline powder of the trihydrate $CdP_2O_6.3H_2O$, by the action of ammonium or alkali dimetaphosphate on a soln. of cadmium sulphate. The water is lost at 150° without otherwise changing the salt, but an alteration occurs at a higher temp. The salt melts at a red heat, and when slowly cooled forms the tetrametaphosphate. 100 parts of water dissolve 3·13 parts of the salt. Both the cadmium and zinc salts are scarcely attacked by acids other than sulphuric acid; and are easily decomposed by molten sodium carbonate, forming sodium dimetaphosphate.

A. Bette obtained a white precipitate which soon coagulated to a resinous mass, and dried to a white powder by mixing ammoniacal soln. of zinc sulphate and vitreous sodium phosphate. The dry precipitate has 6·50 per cent. NH_3, 46·45ZnO, 33·68P_2O_5, and 13·37H_2O, and it was supposed to be a mixture of phosphoric acid with a double phosphate of zinc and ammonium. A. Glatzel prepared **tetrahydrated ammonium zinc dimetaphosphate,** $(NH_4)_2ZnP_4O_{12}.4H_2O$, by treating zinc dimetaphosphate with an aq. soln. of ammonium chloride. It gives off ammonia at 200°, and most of the phosphoric oxide may be volatilized by prolonged heating. The salt also melts to a colourless glass; and it is decomposed by sulphuric acid. 100 parts of water dissolve 1·43 parts of the salt. A. Glatzel prepared **trihydrated ammonium cadmium dimetaphosphate,** $(NH_4)_2CdP_4O_{12}.3H_2O$, in white granules by the action of ammonium chloride on cadmium dimetaphosphate, or of ammonium dimetaphosphate on cadmium chloride. Two-thirds of the water are lost at 150°, and all at 200° without change in its constitution; it dissolves readily in acids. The compound loses ammonia when heated above 200°, and melts to a glass at a bright red heat. The glass is slowly decomposed by boiling acids, and rapidly by fused sodium carbonate.

G. Tammann reported that he had prepared **zinc trimetaphosphate,** $Zn_3(P_3O_9)_2.9H_2O$, by mixing sodium trimetaphosphate with zinc chloride or sulphate. The precipitate separates slowly; 0·1 grm. dissolves in a litre of water at 20°; and it melts to a glass at a dark red heat. A. Wiesler, however, could get only the pyrophosphate; nor did G. von Knorre succeed in verifying G. Tammann's conclusion. T. Fleitmann and W. Henneberg made **sodium zinc trimetaphosphate,** $Zn_2Na_2(P_3O_9)_2$; and A. Wiesler reported that **sodium cadmium trimetaphosphate,** $Na_4Cd(P_3O_9)_2.4H_2O$, is obtained as a flocculent precipitate by mixing 10 grms. of sodium trimetaphosphate with a conc. soln. of 8 grms. of cadmium iodide, and

precipitating with alcohol. It is sparingly soluble in water and insoluble in alcohol.

A. Glatzel prepared **zinc tetrametaphosphate,** $Zn_2P_4O_{12}$, by evaporating a soln. of zinc oxide in one per cent. excess of phosphoric acid, heating the dry mass to redness, and slowly cooling. The powdered mass is washed with cold water. The salt is decomposed by fusion with sodium carbonate ; it is soluble in nitric acid ; dissolved by boiling sulphuric acid ; and forms tetrametaphosphoric acid and zinc sulphide when treated with hydrogen sulphide. The **decahydrated zinc tetrametaphosphate,** $Zn_2P_4O_{12}.10H_2O$, separates in white crystals from dil. soln. of alkali tetrametaphosphate and zinc salts. Part of the water is lost at 100°, and all at 150°. It melts to a clear glass at a red heat ; 1·818 parts of the salt dissolve 100 parts of water ; and it is decomposed by boiling acids. A. Glatzel prepared **cadmium tetrametaphosphate,** $Cd_2P_4O_{12}$, and **decahydrated cadmium tetrametaphosphate,** $Cd_2P_4O_{12}.10H_2O$, in a similar manner. T. Fleitmann found that the former is easily decomposed by a soln. of sodium sulphide. A. Glatzel prepared colourless crystals of **hexahydrated potassium zinc tetrametaphosphate,** $ZnK_2P_4O_{12}.6H_2O$, by the action of potassium chloride on a soln. of zinc dimetaphosphate, and when heated to dull redness, the water is lost and the anhydrous salt is formed without change in the constitution. The salt melts at a strong red heat, and forms on cooling an opaque mass without any dimetaphosphate. It is decomposed by boiling sulphuric acid ; and 1·14 parts of the salt dissolve in 100 parts of water. He also prepared in a similar way, **trihydrated potassium cadmium tetrametaphosphate,** $CdK_2P_4O_{12}.3H_2O$, 0·74 part of which dissolves in 100 parts of water ; hexahydrated **sodium zinc tetrametaphosphate,** $Na_2ZnP_4O_{12}.6H_2O$, and trihydrated **sodium cadmium tetrametaphosphate,** $Na_2CdP_4O_{12}.3H_2O$, which is insoluble in water and more easily decomposed by water than the potassium salt. G. Tammann also reported regular crystals of **sodium zinc octometaphosphate,** $Na_2Zn_3P_8O_{24}$, as a result of melting a mol of sodium ammonium phosphate with a mol of zinc sulphate. It is insoluble in most acids, but soluble in conc. sulphuric acid ; and produces a grey film when treated with alkali sulphides.

J. Müller [6] obtained what was possibly **zinc triphosphate,** $Zn_5(P_3O_{10})_2$, by treating insoluble sodium metaphosphate with a sat. soln. of zinc sulphate at 70°, for a long time, and he made **cadmium triphosphate,** $Cd_5(P_3O_{10})_2$, in a similar way ; and P. Glühmann made it by treating an aq. soln. of sodium triphosphate with a soln. of cadmium sulphate. The product may be a mixture of tetraphosphate and pyrophosphate because the reactions are characteristic of pyrophosphates. It sinters without melting at a red heat, and it then becomes insoluble in acids. The salt is insoluble in water. F. Schwarz prepared prismatic, possibly triclinic crystals of hydrated **sodium zinc triphosphate,** $NaZn_2P_3O_{10}.9\frac{1}{2}H_2O$, by the action of a zinc salt on sodium triphosphate. P. Glühmann made **dodecahydrated sodium cadmium triphosphate,** $Na_3CdP_3O_{10}.12H_2O$, from a cold sat. soln. of cadmium sulphate and the calculated quantity of sodium triphosphate. The mineral *arakawaite* from Arakawa Mine, Akita, Japan, was described by Y. Wakabayashi and K. Komada as a **zinc copper phosphate,** $(Cu,Zn)_6P_2O_{11}.7H_2O$. The dark bluish-green crystals belong to the monoclinic system, and have the axial ratios $a : b : c = 0·7497 : 1 : 1·0245$, and $\beta = 70° 30'$. The sp. gr. is 3·09 ; the hardness $3\frac{1}{2}$; the optic axial angle $2\gamma = 38° 30'$; the indices of refraction $\alpha = 1·618$, $\beta = 1·622$, and $\gamma = 1·658$; and the optical character positive.

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§ 21. Alloys and Intermetallic Compounds of the Calcium and Zinc Families

The alloys of calcium and of barium or strontium with the alkali metals have not been investigated. H. Caron [1] obtained an alloy of sodium and calcium by melting in a well-closed iron crucible an excess of sodium with calcium chloride. When the resulting product is heated in an iron retort, the sodium may be all distilled off. W. Moldenhauer and J. Anderson prepared an alloy of calcium and potassium. A review of our present knowledge of the binary alloys of the alkali, copper, calcium, and zinc families is indicated in Table VI, which shows by a hyphen (—) that the

TABLE VI.—BINARY INTERMETALLIC COMPOUNDS.

	Na	K	Rb	Cs	Cu	Ag	Au	Ca	Be	Mg	Zn	Cd	Hg
Li	0	0	—	—	—	—	—	—	—	0	—	C	C
Na		C	—	—	—	0	C	—	—	0	C	C	C
K			—	—	—	—	—	—	—	0	C	C	C
Rb				—	—	—	—	—	—	—	—	—	C
Cs					—	—	—	—	—	—	—	—	C
Cu						0	0	C	C	C	C	C	—
Ag							0	C	0	C	C	C	—
Au								—	—	C	C	C	—
Ca									—	C	C	C	C
Be										—	—	—	—
Mg											C	C	C
Zn												0	0
Cd													0

alloys have not been investigated; a cipher means that no compound is formed; and a C means that one or more compounds are known. For convenience, mercury has been included in the summary.

Sodium, potassium, and lithium do not unite with magnesium to form a compound. T. L. Phipson [2] made a ductile alloy of magnesium and sodium which decomposed water at ordinary temp. J. Parkinson found the two elements unite at a red heat without incandescence, and form a silvery white alloy which readily decomposes water when the sodium dissolves, and magnesium metal remains. Mixtures of magnesium and sodium separate into two layers at 638° one with between 2 and 97 per cent. of sodium, and the other with up to 3 per cent. of magnesium, Fig. 56. According to T. L. Phipson, magnesium alloys with potassium to form a ductile alloy which decomposes water at ordinary temp.; but D. P. Smith showed that the two elements are almost immiscible when melted, and that the m.p. of neither element is much affected by small additions of the other, Fig. 55. The behaviour of potassium resembles that of sodium towards magnesium, but the solubility of potassium is even less than that of sodium in magnesium. G. Masing and G. Tammann showed lithium and magnesium form two series of mixed crystals above 95 per cent., and below 85 per cent. magnesium, Fig. 54.

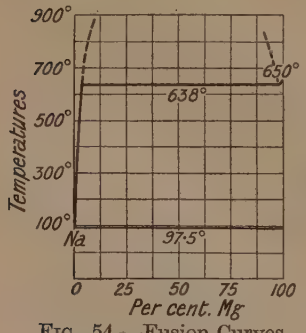

FIG. 54.—Fusion Curves of Lithium-Magnesium Alloys.

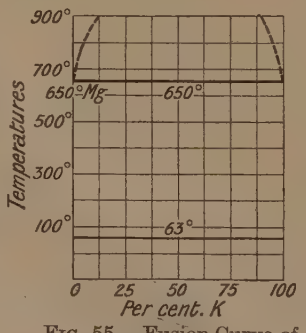

FIG. 55.—Fusion Curve of Potassium-Magnesium Alloys.

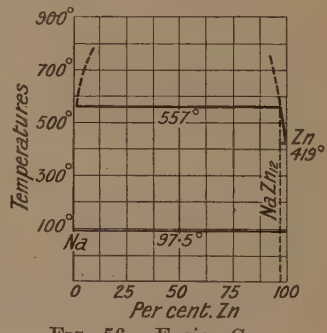

FIG. 56.—Fusion Curve of Sodium-Zinc Alloys.

Both sodium and potassium appear to unite with zinc to form binary compounds, Figs. 56–57. J. L. Gay Lussac and L. J. Thénard,[3] and G. S. Sérullas made an alloy of potassium and zinc. The brittle mass melted at a red heat; oxidized readily in air; and decomposed water, especially in the presence of dil. acids. J. L. Gay Lussac and L. J. Thénard also made an alloy of sodium and zinc. Qualitative experiments on the zinc-sodium alloy were also made by R. Rieth and F. Beilstein,

F. Haber and M. Sack, H. Rose, and C. T. Heycock and F. H. Neville. L. Hulin made the alloy by forcing a stream of sodium under press. into a bath of molten zinc. F. L. Sonnenschein, C. H. Mathewson, N. S. Kurnakoff and A. N. Kusnetzoff studied the alloys of cadmium and sodium; and D. P. Smith those of potassium and cadmium. The general character of the equilibrium curves is shown in Figs. 56 and 57. Certain arrests in the cooling curve are interpreted to mean chemical combination. The provisional formulæ of **potassium zincide** is $KZn_{11 \text{ or } 12}$, and of **sodium zincide,** $NaZn_{11 \text{ or } 12}$, as advocated by D. P. Smith and C. H. Mathewson. Potassium and cadmium alloys give a f.p. curve rising to a maximum at 473°, corresponding with **potassium cadmide,** $Cd_{11 \text{ or } 12}K$, and then falling to a horizontal line at 468° with between 17 and 99 atomic per cent. of potassium. Mixtures represented by points on this line separate into two layers—one rich in potassium, and the other rich in cadmium. There is a doubt whether a slight singularity in the curve between the horizontal line and the maximum for $KCd_{11 \text{ or } 12}$ represents an experimental error or the formation of a compound Cd_7K. R. Kremann and A. Mehr measured the e.m.f. of zinc alloys with potassium for the cell Zn | $KCl_{pyridine}$ | $K—Zn_{alloy}$; and similarly also for Cd | $KCl_{pyridine}$ | $K—Zn_{alloy}$. G. Tammann measured the chemical activity of the potassium alloys with cadmium and with zinc. The curve with sodium and cadmium was shown by N. S. Kurnakoff and A. N. Kusnetzoff to have two maxima corresponding with **sodium cadmides** represented by cubic crystals of Cd_4Na or Cd_5Na freezing at 363°, and octahedral crystals of Cd_2Na freezing at 385°, and with a sp. gr. 5·669 at 20°/4°. There is a horizontal line at 330°, with between 58 and 70 atomic per cent. of sodium. The depression in the f.p. of cadmium observed by G. Tammann, and by C. T. Heycock and F. H. Neville, is too small to appear on the scale of Fig. 59. W. Biltz and C. Haase found 5·650 for the sp. gr. of sodium dicadmide at 25°/4°; and 7·069 for that of the pentacadmide. They also measured the heats of formation of these compounds. According to G. D. Roos, the heat of fusion of sodium cadmide, $NaCd_4$, is 16·9

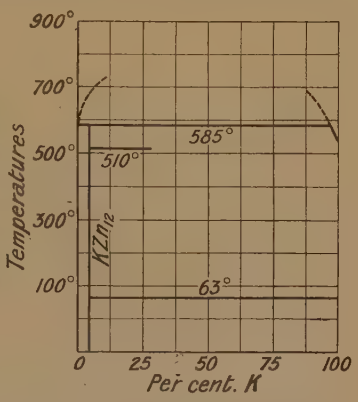

FIG. 57.—Fusion Curve of Potassium-Zinc Alloys.

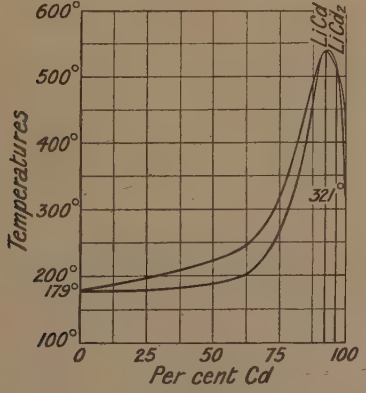

FIG. 58.—Fusion Curve of Lithium-Cadmium Alloys.

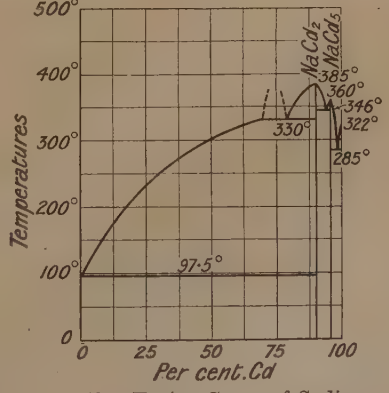

FIG. 59.—Fusion Curve of Sodium-Cadmium Alloys.

Cals. per gram, and of Cd_2Na, 22·8 Cals. per gram. The heats of formation of the two compounds are respectively 60·6 ± 3·5 Cals. per mol, and 30·8 ± 1·6 Cals.

per mol. There is also estimated to be a 10 per cent. dissociation on melting $NaCd_4$ and 5·5 per cent. dissociation on melting $NaCd_2$. G. Tammann measured the chemical activity of sodium alloys with zinc and with cadmium. According to G. Masing and G. Tammann, lithium probably forms two **lithium cadmides,** namely, LiCd, freezing at 505°; and $LiCd_2$, freezing at 541°. The equilibrium diagram is shown in Fig. 58. R. Kremann and P. von Reiningshaus studied the e.m.f. of alloys of sodium with zinc and cadmium.

P. Lebeau [4] has prepared alloys of copper and beryllium by heating a mixture of the two oxides in an electric furnace. The alloy with 1·32 per cent. of beryllium is golden-yellow, and that with 5 per cent. of this metal is yellow, easily polished, does not oxidize in air, and dissolves with difficulty in nitric acid. The alloy with 10 per cent. of beryllium is pale yellow, almost white. The alloys give a f.p. curve, Fig. 61, which shows that the m.p. of copper (1083°) is depressed rapidly to 865° by the addition of beryllium, and α-solid soln. containing up to 10·5 atomic per cent. of beryllium are formed; the f.p. curve then changes its direction and falls less rapidly down to a eutectic at about 840° with 27·3 atomic per cent. of beryllium. The curve then rises to a point of inflection at about 910°, and there is a break at 938°. There is a point of inflection corresponding with **beryllium cupride,** Cu_2Be,

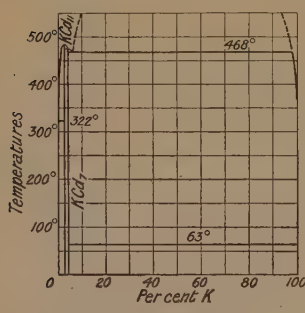

Fig. 60.—Fusion Curve of Potassium-Cadmium Alloys.

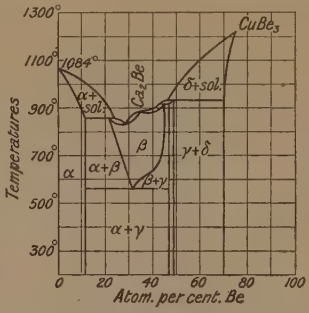

Fig. 61.—Fusion Curve of Beryllium-Copper Alloys.

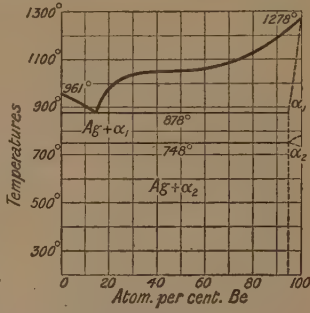

Fig. 62.—Fusion Curve of Beryllium-Silver Alloys.

and breaks at about 910° and 938°. The curve then rises to a point of inflection at 1206° corresponding with $CuBe_3$. β-solid soln. extend from 23·5 to 45·5 atomic per cent. of beryllium; γ-solid soln. from 46·5 to 49 atomic per cent. of beryllium; and δ-solid soln. from 70 to 75 atomic per cent. of beryllium. A mixture of β- and γ-solid soln. extends from 45·5 to 46·5 atomic per cent. of beryllium, and a mixture of γ- and δ-solid soln. from 49 to 70 atomic per cent. of beryllium. The f.p. curve of silver-beryllium alloys is much simpler than is the case with the copper-beryllium alloys. G. Oesterheld found a eutectic at 878° with about 15·3° atomic per cent. of beryllium, and the curve rises to a point of inflection at 92·6 atomic per cent. of beryllium when there is a break representing a compound of unknown composition—$AgBe_n$, Fig. 62.

J. Parkinson [5] prepared an alloy of copper and magnesium by putting magnesium under molten copper, covered with a layer of charcoal; H. N. Warren and others made an alloy by melting the two metals under borax, magnesium, sodium, or potassium chloride, or calcium fluoride. R. E. Slade reduced a mixture of magnesia and carbon in an electric furnace, and absorbed the vapour of magnesium by copper; A. Schmidt, and K. Seubert and A. Schmidt heated a mixture of cuprous chloride and magnesium filings; J. Bogusky electrolyzed fused cryolite with copper electrodes; D. S. Ashbrook electrolyzed mixed soln. acidified with nitric acid—A. Siemens found soln. of the sulphates do not give an alloy. M. Rietz and M. Herold electrolyzed a mixed soln. of a magnesium salt of an organic acid and cupric cyanide. The f.p. diagram of copper and magnesium, Fig. 63, has three eutectics, one with about

9 per cent. of magnesium, melting at about 480° ; one with about 31 per cent. of magnesium, melting at about 552° ; and one with about 70 per cent. of magnesium, melting at about 485°. According to R. Sahmen, the maximum at 797° corresponds with **magnesium cupride,** Cu_2Mg ; and that at 570° with $CuMg_2$. O. Boudouard's compound CuMg has no existence. L. Guillet found that alloys with up to 4 per cent. of magnesium are malleable ; J. Parkinson's report of the brittleness of the alloys is based on experiments with impure materials. M. Mouchel found the alloys have great mechanical strength, and a small electrical resistance ; and L. Aitcheson tested the mechanical properties of the 3 and 13 per cent. copper alloys. G. Tammann and K. Dahl also studied the brittleness of this compound. They observed no gliding planes in the crystals, and noted the compound becomes plastic 50° below its m.p. C. A. Kraus measured the electrical conductivity of magnesium dicupride and hemicupride. O. Boudouard noted the solubility of the alloys in dil. nitric acid : E. Beck, the fixation of nitrogen by the heated alloy ; W. Jenge, and G. Tammann, the chemical activity ; and R. Sahmen, the attack on porcelain by molten alloys with over 10 per cent. of magnesium.

J. Parkinson [6] prepared an alloy of silver and magnesium. S. F. Schemtschuschny studied the f.p. curve, Fig. 64, and obtained a eutectic at 756°, and a maximum at 820° corresponding with **magnesium argentide,** AgMg, and there is a bend in the curve at 492° corresponding with the argentide $AgMg_3$. There is a second eutectic at 469°. W. Smirnoff and N. S. Kurnakoff stated that these two compounds form hylotropic phases, for they melt without decomposition. Silver

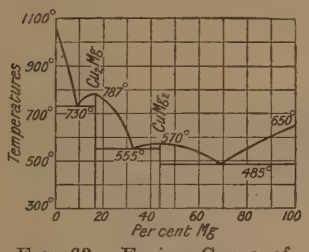

Fig. 63.—Fusion Curve of Magnesium-Copper Alloys.

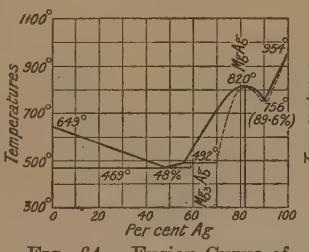

Fig. 64.—Fusion Curve of Magnesium-Silver Alloys.

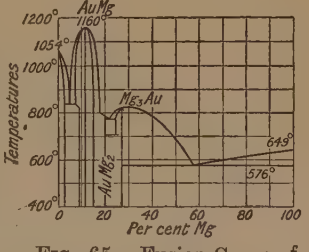

Fig. 65.—Fusion Curve of Magnesium-Gold Alloys.

forms solid soln. with about 28 at. per cent. of magnesium, and the compound AgMg forms solid soln. with 12 at. per cent. of silver, and 16 at. per cent. of magnesium. According to S. F. Schemtschuschny, the crystals of Mg_3Ag belong to the hexagonal system, and have axial ratios $a : c = 1 : 0{\cdot}6965$. W. Smirnoff and N. S. Kurnakoff studied the hardness of the magnesium-silver alloys, and obtained a well-defined minimum corresponding with the compound Mg_3Ag ; at this point there is also a minimum in the electrical conductivity curve, and a maximum in the curve representing the temp. coeff. of the electrical resistance. There was also a sharp maximum in the conductivity curve corresponding with MgAg. K. Bornemann found that freshly cut surfaces of alloys with 57 to 70 at. per cent. of silver are yellow ; the malleability of silver is lowered when alloyed with magnesium ; and alloys rich in magnesium are brittle and decompose water more easily than silver alone. G. Tammann studied the chemical activity of the alloy.

Alloys of gold and magnesium were first made by J. Parkinson,[7] and they were studied in detail by R. Vogel, and G. G. Urazoff. They were made by heating a mixture of the two metals in a graphite crucible under a layer of fused potassium chloride and calcium chloride. M. le Blanc and L. Bergmann observed the formation of the alloy when magnesium was heated with sodium hydroxide to 400° in a gold crucible. The fusion curve is shown in Fig. 65. There is a eutectic at 830°, and a maximum corresponding with the formation of **magnesium auride,** AuMg, between 1150° and 1160° ; a second eutectic occurs at 783°, and a second maximum

at 788°–796° corresponding with $AuMg_2$; a third eutectic occurs at about 772°. and a third maximum between 818° and 830°, corresponding with $AuMg_3$; and a fourth eutectic occurs at about 576°. There is a break in the curve at 796°–798°, corresponding with the formation of Au_2Mg_5. Several solid soln. are formed. G. Tammann studied the chemical activity of the alloy. He argued that in a series of mixed crystals or in a mixture of definite chemical individuals the alloy behaves either as one component or as the other; thus the AuMg-alloy is as noble as gold, and the $AuMg_2$-alloy is as easily attacked as magnesium.

Certain alloys of copper and zinc, used extensively in the arts and crafts, are called brasses; and certain alloys of copper and tin are likewise called bronzes. Copper is the predominant element in brasses and bronzes, and its primary function is to impart toughness and strength to the alloy. The additional elements modify the physical properties—m.p., tenacity, hardness, ductility, sp. gr., electrical resistance, etc.—in certain desired directions. By simply varying the proportions of zinc between 30 and 50 per cent., alloys may be obtained presenting such diverse qualities that the different members of the series appear to represent different metals. The history [8] has been previously discussed; the term *asem* was employed in the third-century Egyptian papyri for an alloy of copper and tin. There is a chapter headed *De compositis brandisii* in the eighth-century book *Compositiones ad tingenda*, which deals with the manufacture of bronze, and this has been taken to show that the term bronze is derived from Brindes, a synonym for Brandusium (Brindisi), a town noted in Pliny's day for its bronze mirrors. There is, however, no general agreement as to the origin of the term *bronze*. The term *brass* seems to be derived from *braes*, an old English word for an alloy of tin and copper, and which later came to be used for alloys of zinc and copper. The old brasses resembled the modern metal in composition and analyses have been given by C. J. B. Karsten,[9] C. C. T. F. Göbel, J. A. Phillips, and many others.

In a report: [10] *The Nomenclature of Alloys*, it is recommended that the term *brass* be used as an abbreviation for the words "copper-zinc alloys containing over 50 per cent. of copper." If the alloy contains a third metal intentionally added, the name of that is applied as a prefix—*e.g.* an alloy with one per cent. of tin, 29 of zinc, and 70 of copper would be called *tin-brass*; and the so-called German silver, copper 50, zinc 25, and nickel 25, becomes *nickel-brass*. If additional metals are present, their names can be similarly prefixed, or the term *complex-brass* can be employed. The term *bronze* is likewise to be used as an abbreviation for "copper-tin alloys containing over 50 per cent. of copper." The presence of a third metal intentionally added is indicated as in the case of brass; and likewise for *complex-bronzes*.

There are many varieties of brass, and several have received special trade names. A brass suitable for rolling and drawing contains approximately 30 per cent. of zinc, and one rather less ductile has 33 per cent. of zinc; brass for naval work has about 37 per cent. of zinc and one per cent. of tin, it resists the corrosive action of sea-water rather better than ordinary brass, and it is harder. Lead is sometimes added to brass to facilitate its being turned or machined. Few brasses used for engineering work contain over 40 per cent. of zinc because of their low ductility. Table VII represents the composition of a number of varieties of brass.

Small quantities of iron harden and strengthen copper alloys, the use of ferro-manganese for the same purpose was patented by P. M. Parsons [11] in 1876. The alloys hardened by the addition of ferro-manganese ranged from the true brasses to the true bronzes of the gun-metal type. The manganese acts as a deoxidizer, and causes the iron to alloy more readily with the metal. If more manganese is used, it has a hardening and strengthening effect like iron, but not so pronounced. The alloy has a relatively high resistance to the corrosive influence of sea-water. Sand castings of **manganese brass** were found to be impracticable and the first castings were true bronzes fortified with a little manganese, but on account of the greater cost of tin these alloys were more expensive than brasses. P. M. Parsons later found that the addition of a little aluminium to the manganese brasses with 40 to 45 per cent. of zinc, enable sand castings to be made equal to, if not superior to, the more costly bronze, and, owing to a confusion in the use of terms, **manganese bronze**

was applied to both tin and zinc alloys. The best brands of manganese bronze on the market are in reality high-grade brasses. With 55 to 60 per cent. of copper and 40 to 45 per cent. of zinc with small amounts of tin, manganese, aluminium, etc., along with a hardener—usually iron—*e.g.* the U.S. Navy Department's specification manganese bronze contains: copper, 56–58 per cent.; zinc, 40–42 per cent.; and not more than 1·0 per cent. of tin, 0·5 per cent. of aluminium, 0·3 per cent. of manganese, and 0·10 per cent. of lead. Manganese bronzes of varying tensile strength and ductility can be obtained by varying the proportions of copper and zinc. There are two main varieties—one is used for rolling and drawing and contains no aluminium, and the other is used for sand castings and contains aluminium.

TABLE VII.—SOME COPPER-ZINC ALLOYS.

Alloy.	Zinc.	Copper.	Remarks.
Antifriction metal	85	5	Antimony, 10.
Foundry metal	75	—	Tin, 25.
Vaucher's bearing alloy	75	—	Tin, 18; Pb, 4·5; Sb, 2·5.
Manganese bronze	56–58	42–40	Al, Mn, Sn, and Pb, about 2.
Mosaic gold	55–52	45–48	Bath metal has 45Zn, 55Cu.
Brazing solder	50	50	Other proportions are used.
Delta metal	43	55	Iron, 1 to 2.
Muntz metal	40	60	
Sterro-metal	38	60	Iron, 1 to 2.
Admiralty naval brass	37	62	Tin, 1.
Common brass	33	67	
Cartridge brass	30	70	
White metal	22	54	Nickel, 24.
German silver	20	50	Nickel, 30.
Dutch metal	20	80	Also Mannheim gold.
Similor	16·7	83·3	
Tombac	15·5	84·5	
Imitation yellow gold	15	85	Tin up to one per cent.
Prince's metal	14	86	
Oreide	10	90	
Red tombac	8	92	
Pinchbeck	6·4	93·6	
Viennese tombac	2·8	97·8	
Admiralty gun metal	2	98	Tin up to 10 per cent.
British coinage	1	95	Tin up 4 to per cent.
Imitation red gold	4	96	Tin up to one per cent.

The effect of *silver* and *gold* on brass has been studied by L. Guillet; of *aluminium*, by L. Guillet, O. Bauer, J. Czochralsky, W. Rosenhain, J. L. Haughton, and K. E. Bingham; of *manganese*, of *chromium*, of *magnesium*, of *cadmium*, and of *silicon*, by L. Guillet; of *antimony*, by J. Czochralsky; of *arsenic*, by R. T. Rolfe; of *iron*, by L. Guillet, F. Johnson, and O. Smalley; of *cobalt*, L. Guillet, and S. Pile; of *nickel*, by L. Guillet, and S. Pile; of *tin*, by L. Guillet, and W. Campbell, see bronze; of *lead*, by L. Guillet, and A. Kessner; of *phosphorus*, by A. Portevin; of *cerium*, by L. W. Spring; and of *sulphur*, by S. Pile.

In the older method of making brass, roasted calamine, or furnace calamine, mixed with charcoal and granulated copper, was heated in a crucible; and also zinc oxide was heated with copper and charcoal under similar conditions. Brass is usually made by fusing the two metals in a graphite crucible, the copper being placed above the zinc.[12] When copper is exposed to the vapour of zinc it is completely penetrated and brass is formed. The so-called Lyons gold lace was made by exposing rods of copper to the vapour of zinc and when the surface had been converted into brass, the rods were drawn into wire. When a copper coin is placed in a crucible above a mixture of charcoal and zinc oxide, and moderately ignited, the copper is converted into brass without spoiling the impression on the coin. P. Lebeau,[13] and G. L. J. de Chalmot produced some brass by the action of zinc on cupric silicide, Cu_2Si; and B. Neumann, and F. von Kügelgen, by reducing a mixture of zinc

chloride and cupric oxide with calcium carbide. W. Spring, and G. Masing made alloys by compressing mixtures of the powdered elements. According to W. Meissner, when a soln. of copper sulphate in 20 parts of water is precipitated by zinc, the first black flakes which separate are an alloy of copper and zinc; and F. Mylius and O. Fromm also made similar observations. R. Böttger noted the formation of a film of brass when copper is dipped in a soln. of sodium zincate. H. Weiss, and O. H. Hudson studied the reciprocal penetration of zinc and copper at temp. below 419°. F. M. Raoult found that brass is formed when a copper plate in contact with a zinc wire is dipped in a soln. of zinc sulphate. F. Mylius and O. Fromm [14] observed that a zinc anode in a soln. of a cupric salt is at first blackened owing to the formation of a copper-zinc alloy. C. B. Jacobs, W. D. Bancroft, K. Norden, J. L. R. Morgan, G. McP. Smith, S. P. Thompson, T. J. Baker, F. W. Croucher, L. Houllevigne, F. Kunschert, S. O. Cowper-Coles, R. Namais, F. Sauerwald, F. Peters, A. L. Ferguson and E. G. Sturdevant, G. Langbein, J. Stark, F. Spitzer, etc., have studied the electrolytic deposition of brass from aq. soln. of zinc and copper salts. W. H. Walenn, working with an electro-brassing soln. containing potassium cyanide and ammonium tartrate, at a temp. a little above 0°, obtained nearly pure zinc on the cathode; as the temp. was raised, the deposit changed in tint, becoming silvery white, and then acquired a yellow colour. He suggested that M. Prat's new element *lavœsium* is the silvery-white deposit. O. Meyer deposited brass from an alcoholic soln. of the two salts; and R. Lorenz, from fused cupric and zinc chlorides.

T. Svedberg prepared brown **colloidal brass**—brass methyl-alcosol by his process previously described—**2.** 23, 10. O. Ohmann made *brass wool*. M. R. Andrews found that the **X-radiograms** of zinc-copper alloys show three structures: those with 0–0·40 per cent. of zinc have the face-centred cubic lattice of copper; those with 40–50 per cent. of zinc have mixed face-centred and centred cubic lattices; those with 50–70 per cent. of zinc have a nearly pure centred cubic lattice; those with 70–80 per cent. of zinc have a mixture of the centred cubic lattice and another probably rhombohedral; those with 80–90 per cent. of zinc have almost the pure rhombohedral form; and those with 90–95 per cent. of zinc have a mixture of the rhombohedral and the hexagonal zinc lattices. E. C. Bain also studied the X-radiograms of these alloys.

Many copper-zinc alloys have been symbolized by chemical formulæ as if the mixtures were chemical individuals—*e.g.* F. C. Calvert and R. Johnson,[15] J. H. Croockewit, T. Matsuda, J. W. Mallet, etc. E. S. Shepherd failed to find any clear evidence of the formation of definite compounds of copper and zinc, and he stated that all the alloys of these metals are solid soln. A. P. Laurie, W. Guertler, G. Charpy, M. Herschkowitsch, and T. J. Baker, from measurements of certain physical properties, inferred the existence of a **zinc cupride,** Cu_2Zn_3, and possibly Cu_2Zn. The compound Cu_2Zn is probably formed at 905°, and Cu_2Zn_3 at 830°. There may be other compounds, but their composition has not been established. N. A. Puschin [16] believes that in its alloys, copper behaves like a univalent element in the first group of the periodic table. The thermal and other properties of the copper-zinc alloys have been the subject of many investigations. The general f.p. curve is illustrated by Fig. 66, where $\alpha_{liq.}$ is employed as an abbreviation for a mixture of α-solid plus liquid; similarly for $\beta_{liq.}$; etc. The symbols α, β, γ, δ, ϵ, and η represent the six solid soln. of the two metals. The liquidus curve has six branches corresponding with the six solid phases represented by α, β, γ, δ, ϵ, and η. Alloys with less than 30 per cent. of zinc always contain the α-solid soln., and alloys with up to 37 per cent. of zinc may contain nothing but the α-phase, but with alloys over 30 per cent. zinc, the β-phase may also be present. The equilibrium conditions for these and other phases are indicated in the diagram. When a molten brass containing, say, 70 per cent. of copper is cooled the α-solid soln. separates out, the first portions are much richer in copper than the later portions, and the last portions to freeze out are richest in zinc, but are still within the range of the α-soln. The polished surface

of the solid metal shows under the microscope a number of primary red cores surrounded by the lighter coloured brass—the cores contain about 85 per cent. of copper, the lighter portions have about 65 per cent. of copper, so that the whole of the heterogeneous mass contains the α-solid soln. When this brass is annealed the cored structure disappears, because the zinc slowly diffuses from the parts where it is most conc. to the parts poorest in zinc. A molten brass with about 60 per cent. of copper furnishes both β- and α-solid soln. when it is cooled; when annealed between 400° and 470°, the β-solid soln. is gradually absorbed by the primary β-solid soln. An alloy containing 40 per cent. of zinc—Fig. 66—rapidly cooled from 880°, contains

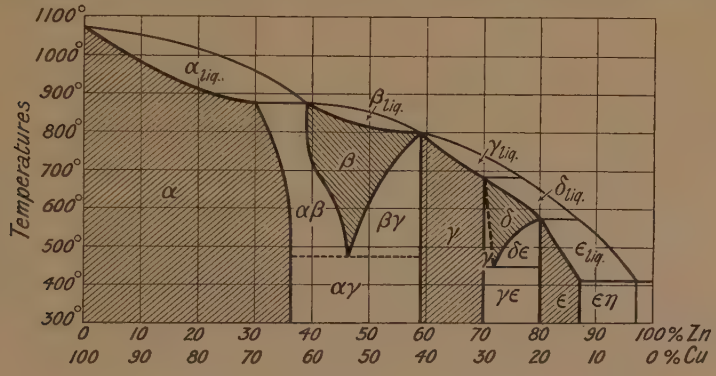

FIG. 66.—Equilibrium Diagram of Copper-Zinc Alloys.

the β-phase; if annealed to 650° and rapidly cooled, it contains the solid phase α and β side by side; and if annealed at 400°, the solid contains the α and γ phases.

Brasses with the α-phase predominant are soft, with a high tensile strength and ductility; the appearance of the β-phase makes the brass harder, stronger, and less ductile. Expressing the percentage composition as a weight ratio—copper : zinc, typical commercial 70 : 30-brass or cartridge brass has a single homogeneous solid soln., the α-constituent. The alloy is very ductile, and can undergo severe cold-working without cracking, but cannot be rolled at a red heat without difficulty. In the 60 : 40-brass, the α-constituent is accompanied by the β-solid soln., which increases from zero to unity as the percentage of zinc increases from 36·5 to 46·5. The β-constituent is plastic at high temp., and moreover, the ratio of $\beta : \alpha$ increases with rise of temp., and the original proportion is restored on cooling. The plastic β-constituent enables brass to be rolled, stamped, or extracted at a red heat; and the product can be readily machined when cold. F. Johnson has made a special study of the effect of cold rolling on β-brass. L. Guillet and M. Ballay studied the effect of work—*écrouissage*—on the critical points of brass; and W. Fränkel and H. Becker, the speed of formation of α and β brasses.

The **colour** of the series of copper-zinc alloys has been studied by R. Mallet,[17] T. Turner, H. Behrens, E. S. Shepherd, etc. Expressing the proportions as an atomic ratio Cu : Zn, R. Mallet reported :

Reddish-yellow.	Yellowish-red.	Pale yellow.	Deep yellow.	Silver-white.	Light grey.	Dark grey.
10 : 1 to 7 : 1	6 : 1 to 4 : 1	3 : 1	2 : 1 to 1 : 2	8 : 17 to 1 : 2	8 : 19 to 8 : 23	1 : 3 to 1 : 5

The colours of the copper-zinc alloys, with increasing proportions of zinc, pass from the yellowish-red of the 1 to 9 per cent. alloys to the yellow of the 20 to 30 per cent. alloys, the yellowish-red of the 50 per cent. alloys to the pinkish-grey of the 50 to 56 per cent. alloys, the silvery-white of the 58 to 66 per cent. alloys, to the bluish-grey of alloys with over 70 per cent. of zinc. The colour of the solid phases thus appears to be: α-phase (copper 100–63 per cent.), red; β-phase (54–51 per

cent.), reddish-yellow ; γ-phase (40–30 per cent.), silvery-white ; and ϵ-phase (20–13 per cent.), bluish-grey. O. Bauer and H. Arndt observed no liquation or segregation in brasses with 28 and 37 per cent. zinc. The **minute structure** has been studied by F. H. Storer, E. S. Shepherd, A. Portevin, G. Charpy, T. T. Cocking, F. Korber and P. J. H. Wieland, J. L. Haughton and K. E. Bingham, L. Révillon and P. Beauverie, F. Johnson, H. M. Brayton, J. S. G. Primrose, S. Pile, etc. ; the **fracture** by R. Mallet, E. Maey, E. S. Shepherd, G. Charpy, etc. Further, G. D. Bengough and O. F. Hudson, F. Dörinckel and J. Trockels, H. Behrens, H. Moore and S. Beckinsale, P. Breuil, etc., have studied the effect of the annealing temp. on the grain-size of the metal. The effect of annealing and rolling on the **X-radiograms** of the brasses has been studied by S. Nishikawa and G. Asahara. The **specific gravity** was determined by R. Mallet, E. Maey, T. G. Bamford, E. S. Shepherd, R. Hennig, etc. R. H. Weber gave for the sp. gr. at 17°/17°, for alloys with

	100	88·67	78·53	66·53	50·85	41·97	25·95	9·74	0% Cu
Sp. gr. . .	8·997	8·700	8·573	8·444	8·235	8·128	7·744	7·272	7·024

A. Riche inferred the formation of a compound Cu_2Zn_3 from the brittleness and the sp. gr. curves of the copper-zinc alloys. R. H. Weber also inferred the formation of a compound CuZn from the sp. gr. curve. R. J. Anderson and E. G. Fahlman, and F. Johnson and W. G. Jones studied the linear shrinkage in casting brass. G. Tammann and K. Dahl found that while brass at ordinary temp. shows good gliding planes, it becomes plastic about 20° below the m.p. The **specific volume** has been determined by E. Maey, C. Upthegrove and W. C. Harbert, P. Braesco, and W. C. Roberts-Austen ; the **hardness,** by H. Behrens, C. H. Desch, P. Ludwik, J. F. Springer, F. W. Harris, F. Auerbach, F. C. Calvert and R. Johnson, E. S. Sperry, A. Portevin, G. A. Dick, E. Maey, D. Meneghini, W. H. Bassett and C. H. Davis. Breaks in the hardness curve of the copper-zinc alloys led N. S. Kurnakoff and S. F. Schemtschuschny to infer the existence of a compound Cu_2Zn. G. Charpy and H. Behrens' observations on the microscopic structure and hardness of copper-zinc alloys led them to infer the formation of a number of copper-zinc compounds—Cu_2Zn, $CuZn$, $CuZn_2$, $CuZn_4$. J. Traube studied the capillary angle. T. Turner and M. T. Murray, and D. Meneghini showed that the hardness of annealed copper-zinc alloys gives a maximum when 33 to 34 per cent. of copper is present ; the **tensile strength** was measured by G. Charpy, P. Ludwik, E. S. Shepherd, W. C. Roberts-Austen, M. Hanszel, W. C. Unwin, F. Dörinckel and J. Trockels, G. D. Bengough and O. F. Hudson, H. M. Brayton, L. Guillet, A. le Chatelier, E. S. Sperry, G. A. Dick, A. E. Tucker, O. Smalley, etc. ; the **ductility**, by A. Guettier, C. J. B. Karsten, C. Karmarsch, E. Maey, W. C. Roberts-Austen, L. Guillet, G. Charpy, H. Behrens, A. Portevin, C. Barus, H. Tomlinson, etc. ; and the **elastic limit,** by G. Charpy, H. Behrens, E. S. Sperry, etc. F. Dörinckel and J. Trockels studied the **impact test.** According to L. H. Adams, E. D. Williamson, and J. Johnston, the **compressibility** of brass (61·76Cu, 35·92Zn, 2·26Pb, 0·05Fe) is $0{\cdot}89\times10^{-6}$ per megabar, and for the change in vol. δv per c.c. between press. p_0 and p, they found $\delta v=0{\cdot}5\times10^{-4}+0{\cdot}875\times10^{-6}(p-p_0)$. E. Madelung and R. Fuchs gave $0{\cdot}90\times10^{-6}$ megabars per sq. cm. S. Lussana, W. Owens, and F. Dörinckel and J. Trockels measured the compressive strength of brasses. E. H. Amagat gave 0·00000953 for the coeff. of cubical compressibility : and 0·3275 for **Poissan's ratio ;** and he gave 10,851 kgrms. per sq. mm. for the **modulus of elasticity ;** W. Voigt gave 9220 kgrms. per sq. mm. The elastic modulus has also been measured by E. Weston, A. Gray, V. J. Blyth, and J. S. Dunlop, F. C. Lea and co-workers, G. Wertheim, G. Searle, N. Katzenelsohn, M. Baumeister, etc. F. Kohlrausch and E. H. Loomis found that the modulus of elasticity falls with a rise of temp. such that $E=E_0(1-0{\cdot}000485\theta-0{\cdot}00000136\theta^2)$; and A. Gray, V. J. Blyth, and J. S. Dunlop found the **viscosity** increased with a rise of temp. K. Honda and S. Konno gave $1{\cdot}55\times10^8$ at 20° for the coeff. of normal viscosity of rolled 59 : 39 brass at 20°.

R. Stribeck found the **brittleness** rises from 0·03 to 0·10 per cent. when the temp. rises from 300° to 500°. R. H. Thurston, and E. Grüneisen measured the **torsion modulus**. A. Masson, A. Kundt, and G. Wertheim have measured the **velocity of sound** in brass. The effects of annealing, cold work, etc., on the properties have been studied by F. Körber and P. J. H. Wieland, A. E. White, etc.

The **melting point** of copper was found by J. F. Daniell [18] to decrease with the addition of increasing proportions of zinc—*vide* Fig. 66. G. Charpy gave :

Per cent.	100	90·5	80·3	69·5	60·2	51·0	39·7	31·0	25·1	20·4	0
M.p.	1054°	1020°	1000°	945°	880°	852°	812°	790°	700°	592°	415°

C. Féry found that when brass with 37 per cent. of zinc is heated in the electric furnace, at 1100°, the zinc is fractionally distilled. H. Moissan and A. J. P. O'Farrelley also studied the fractional distillation of zinc from the zinc-copper alloys. F. Braun observed the **volatilization** of zinc when a brass wire is heated by an electric discharge ; and W. Crookes, the volatilization of zinc from a cathode in a vacuum tube. L. Guillet and M. Ballay studied the **vapour pressure** of the zinc in these alloys, and found Raoult's law is not applicable. The **coefficient of thermal expansion** was measured by A. L. Lavoisier and P. S. de Laplace, P. Hidnet, W. Roy, A. Matthiessen, G. R. Dahlander, etc. H. Fizeau found 0·00001859 between 0° and 40° ; H. le Chatelier, 0·0000225 at 707° ; and F. Henning, for a brass with 7·5Cu, 27·7Zn, 0·3Sn, 0·5Pb, an expansion of 0·001879 between 0° and 100°. R. S. Willows found the **thermal conductivity** of brass to be about three times as great as for copper. L. Lorenz, T. Turner and D. M. Levy, A. Berget, G. Glage, F. Weber, N. Eumorfopoulos, F. E. Neumann, etc., have measured the thermal conductivity of brass. G. Wiedemann found the relative conductivity to be :

Cu : Zn	100·0	8 : 1	6·5 : 1	4·7 : 1	1 : 1	0 : 100
Rel. cond.	73·6	27·3	29·9	31·1	25·8	28·1

At 18°, C. H. Lees found a conductivity of 0·260 ; at 0°, 0·254 ; at —80°, 0·223 ; and at —160°, 0·181. F. Weber gave 0·791 for the **specific heat** of brass. F. Dörinckel and M. Werner obtained the results indicated in Table VIII ; there is a

TABLE VIII.—THE SPECIFIC HEAT OF ZINC-COPPER ALLOYS.

Cu per cent.	Temperature.								
	20°	100°	232°	327°	400°	500°	600°	700°	800°
99·82	0·0922	0·0941	0·0972	0·0995	0·1010	0·1036	0·1059	0·1083	0·1106
84·80	0·0922	0·0944	0·0977	0·1002	0·1021	0·1050	0·1071	0·1098	0·1125
70·96	0·0916	0·0942	0·0972	0·1009	0·1032	0·1063	0·1090	0·1127	0·1159
66·42	0·0909	0·0937	0·0980	0·1011	0·1034	0·1069	0·1099	0·1136	0·1168
62·96	0·0902	0·0940	0·0998	0·1044	0·1070	0·1122	0·1168	0·1212	0·1254
57·28	0·0895	0·0951	0·1038	0·1102	0·1145	0·1224	0·1283	0·1356	0·1418
53·51	0·0892	0·0955	0·1059	0·1134	0·1191	0·1270	0·1349	0·1428	0·1506

break near 460°, increasing in magnitude as the proportion of zinc increases. R. Schenck measured the ratio of the thermal and electrical conductivities. T. J. Baker could detect no heat change in the formation of brass with 0 to 30 per cent. of copper ; between 30 and 60 per cent. of copper, the **heat of formation** gradually rises to 46 Cals. per gram of alloy ; and gradually falls with increasing proportions of copper. A maximum in the curve corresponds with the compound Zn_2Cu, and a second smaller maximum with CuZn ; A. Galt also found a maximum corresponding with Cu_2Zn_3. M. Herschkowitsch showed that the errors of experiment are large in comparison with the smallness of the magnitude being measured ;

and J. H. Gladstone discussed the effects of variations in the nature of the products of the reaction on the result.

B. Walter [19] studied the **spark spectrum** given by the discharge between brass electrodes. R. Emden found the emission of light from brass begins at 405°. H. Rubens and R. Hagen studied the effect of temp. on the **emission of light.** The absorption and radiating power of brass for Hertz's waves was studied by J. R. von Geitler; while H. Knoblauch studied the **polarization angle** and the abnormal **dispersion** of brass for heat rays. W. G. Hankel found that an illuminated brass plate in water is first electropositive and then electronegative. W. Hallwachs found a brass plate is **photoelectric,** for when illuminated by the arc-light it becomes electrically positive. R. Hamer found the limiting frequency for the photoelectric effect to be $\lambda=3426\pm75$. B. Sabat found that the electrical conductivity of brass is raised by exposure to the radiations from **radium rays.** J. J. Thomson found that no radioactivity is induced by radium rays. E. Salles measured the diffusion coefficient for ionized gases. The ionization of air was found by J. Borgman to be stronger with brass than with copper.

J. Kinsky [20] could detect no transport of either metal relative to the other when an electric current is passed through brass. J. Haas measured the specific **electrical conductivity** in rec. ohms, and the specific **electrical resistance** in ohms, of zinc-copper alloys at 0°, and found:

Zn per cent.	0	0·71	5·51	20·29	34·23	46·85	99·53
Sp. resist.	0·01584	0·01833	0·03010	0·05064	0·06302	0·04314	0·05883
Temp. coeff.	0·004322	0·003725	0·002383	0·001639	0·001579	0·003105	0·0038
Sp. conduct.	63·13	54·56	33·22	19·75	15·87	23·18	17·00

The curve for the sp. resistance rises rapidly until 5 per cent. of zinc is present, and it then rises more slowly until 34 per cent. of zinc is present, when it falls rapidly until 47 per cent. of zinc is present. The temp. coeff. falls rapidly until 5 per cent. of zinc is present, and afterwards more gradually; the fall is nearly constant with between 17 and 30 per cent. of copper; and it then steadily rises until 47 per cent. is present. E. F. Northrup measured the resistance of solid and molten brass; and R. Schenck, the ratio of the thermal and electrical conductivities.

According to A. Matthiessen and C. Vogt, the conductivity of alloys of hard-drawn wires between 0° and 100°, when the conductivity of silver is 100 units, is $60{\cdot}376-0{\cdot}14916\theta+0{\cdot}000247\,3\theta^2$ for alloys with 5·03 per cent. of zinc; $46{\cdot}934-0{\cdot}095947\theta+0{\cdot}000142\,3\theta^2$ for alloys with 10·88 per cent. of zinc; $21{\cdot}298-0{\cdot}040029\theta+0{\cdot}000038\,32\theta^2$ for alloys with 23·61 per cent. of zinc; $21{\cdot}708-0{\cdot}027632\theta+0{\cdot}000026\,98\theta^2$ for alloys with 29·45 per cent. of zinc; and $21{\cdot}793-0{\cdot}029939\theta+0{\cdot}000029\,16\theta^2$ for alloys with 42·05 per cent. of zinc. Other observations on the electrical conductivity of copper-zinc alloys were made by W. H. Mordy, G. Charpy, R. H. Weber, F. Weber, F. E. Neumann, G. Wiedemann, A. Oberbeck and J. Bergmann, H. le Chatelier, A. Berget, L. Lorenz, R. Benoit, O. D. Chwolson, H. Tomlinson, N. A. Puschin and W. Rjaschsky, L. Norsa, W. Fränkel, and H. Becker, etc. R. S. Willows observed no difference in the conductivity of brass for continuous and alternating currents at the temp. of liquid air, of liquid carbon dioxide, at 20°, and at 100°. According to D. Goldhammer, the resistance of brass in a magnetic field was not appreciably changed. W. Guertler argued that the minimum in the electrical conductivity curve corresponding with Cu_2Zn cannot be accepted as evidence of the existence of a compound, but a maximum in the curve indicates the presence of a compound of unknown composition; J. Haas found a maximum in the sp. resistance curve and a minimum in the temp. coeff. corresponding with Cu_2Zn; A. Matthiessen and C. Vogt's, and R. H. Weber's observations also lead to the assumption that compounds are present; C. Liebenoff's observations indicated the formation of CuZn; and H. le Chatelier's of $CuZn_2$. E. Bornemann and K. Wagenmann obtained a minimum in the electrical conductivity curve of the molten metal corresponding with Cu_2Zn_3, showing that

this compound probably exists in the soln. A. Jaamaa and Y. E. G. Leinberg measured the resistance of powdered brass mixed with marble.

The **potential difference** of alloys of copper and zinc was measured by W. E. Ayrton and J. Perry [21] towards water (—0·231 volt); dil. sulphuric acid, 1 : 5 (—0·016 volt); conc. soln. ammonium chloride (—0·348 volt); aq. soln. sodium chloride, sp. gr. 1·18 at 20·5° (—0·435 volt); and a conc. soln. of alum (—0·014 volt). The potential towards cyanide soln. was investigated by F. Spitzer. W. D. Bancroft, J. L. R. Morgan, J. Trowbridge and E. K. Stevens, C. Liebenoff, and H. E. Armstrong, measured the **electromotive force** against platinum in water, and in dil. sulphuric acid; E. Branley, the e.m.f. against copper in dil. sulphuric acid; M. Herschkowitsch, F. Haber, and W. Reinders, the e.m.f. against amalgamated zinc in a soln. of zinc sulphate; S. P. Thompson, against carbon in a soln. of potassium cyanide; H. Pellat, against gold; W. E. Ayrton and J. Perry, against carbon, zinc, tin, lead, iron, and platinum. N. A. Puschin found breaks in the e.m.f. curve of zinc-copper alloys in N-$ZnSO_4$ corresponding with the compounds Cu_2Zn, $CuZn$, $CuZn_2$, and $CuZn_8$. A. P. Laurie, and M. Herschkowitsch also inferred the existence of definite compounds—Cu_2Zn, etc., from the breaks in the e.m.f. curves. F. Sauerwald measured the e.m.f. of copper-zinc alloys against soln. of zinc chloride. G. Tammann studied the difference in the potentials of alloys prepared by electrodeposition and by fusion. P. W. Bridgman measured the **thermoelectromotive force,** or the Seebeck effect, of brass wires, one in the normal state and the other under a tension of 2800 kgrms. per sq. cm. At 52°, $E=(0{\cdot}00022T-0{\cdot}0_73T^2)\times10^{-6}$ volts; at 77°, $E=(0{\cdot}00013T-0{\cdot}0_712T^2)\times10^{-6}$ volts; and at 94°, $E=(0{\cdot}00047T-0{\cdot}0_75T^2)\times10^{-6}$ volts. E. Sedström measured the **Peltier effect** with copper-zinc alloys. R. H. Weber studied the **magnetic susceptibility** of the brasses and found a maximum $-5{\cdot}3\times10^{-6}$ with the composition $CuZn_2$, the compositions Cu_2Zn and $CuZn$ are not clearly marked on the curve, but there are changes in the direction of the curve at approximately Cu_2Zn_3 and $CuZn_3$. L. H. Manhall and R. L. Sanford discussed the magnetic susceptibility of ferruginous brasses.

T. G. Bamford and W. E. Ballard [22] have discussed the action of different gases on brass. When brass is heated in **air,** it acquires a series of colours from surface oxidation. L. Löwenherz showed that it becomes pale gold when heated to 281° for 15 mins., golden-yellow at 341°, and passes through a series of orange and pink colours changing to green. The coloration, said H. Schwarz, is due to the formation of a film of cuprous oxide which is removed by treatment with a conc. soln. of sodium chloride. H. Behrens found pre-treatment of the zinc-copper alloy with dil. sulphuric acid favours the production of the heat films. E. Jordis and W. Rosenhaupt found that at 220° brass with 90 per cent. copper is more rapidly attacked by moist than by dry **oxygen,** and there is a break in the curve which represents the relation between the rate of attack, and the composition which led to the inference that a compound Cu_3Zn is present in the alloy. G. Tammann and W. Köster studied the formation of films on brasses of different composition when warmed in air. F. Schulze-Berge found that brass acquires a negative charge when exposed to **ozone,** and coupled with brass in air; with **ammonia** or **hydrogen** the charge is positive. T. G. Bamford and W. E. Ballard found that hydrogen is absorbed in relatively large quantities by 70 : 30 brass between 500° and 900°, and that most of this gas is retained on cooling. G. Guillemin and B. Delachanal observed the absorption of hydrogen, **methane, carbon monoxide,** and **carbon dioxide** by brass. R. B. Warder reported that when brass is heated to redness in a stream of hydrogen for several hours, the rate of loss of weight diminishes much more rapidly than corresponds with the whole quantity of zinc present. A. Bobierre, and A. R. Haslam made observations on the action of hydrogen on heated brass; and A. Ledebur reported that when brass containing sulphur is heated in a stream of hydrogen, no hydrogen sulphide is formed, showing that the sulphur is probably combined with the zinc and not with the copper or tin.

J. Pintsch noted that brass is more resistant than copper towards the exhaust gases of gas engines. U. Kreusler observed that brass is not attacked by dry **chlorine,** but is attacked by the moist gas. M. Herschkowitsch found an aq. soln. of **bromine** attacks brass.

T. Ihmori estimated that $0{\cdot}27\times10^{-6}$ grm. of **water** per sq. cm. condenses on a clear surface of brass. A. Wagner found that in the absence of carbon dioxide water is without action on brass, or at the most the action is very feeble. J. H. Aberson found that water dissolves much zinc from brass—zinc oxide is first formed, and this is dissolved by the absorbed carbon dioxide, and he added that filters for soft water should be constructed without brass. X. Rocques observed that water in the presence of oxygen, and of compounds of nitrogen or ammonium salts, attacks brass more strongly than copper.

A. T. Lincoln and co-workers, F. Sauerwald, J. H. Reedy and B. Feuer, S. D. Whyte and C. H. Desch, H. W. Bröundson, P. Davidson, A. S. Cushman, A. A. Bado and R. A. Trelles, R. B. Abrams, and P. E. Howe have studied the corrosion by **salt solutions** of copper-zinc alloys and of some complex brasses when used as anode in soln. of electrolytes, as well as the chemical corrosion of these metals. The metals were annealed at 400°. In general, the composition of the corrosion product with alloys with 50 per cent. of copper upwards is the same as that of the test-piece, but with lower proportions of copper, the corrosion product is virtually zinc. Otherwise expressed, the α, $\alpha+\beta$, and the β-brasses yield corrosion products with the same composition as the brass; the presence of γ-crystals causes a marked decrease in the amount of corrosion; while the $\gamma+\epsilon$ and $\epsilon+\eta$ brasses yield a corrosion product of zinc. The results with the tin-brasses were virtually the same as with zinc-brasses. The results with a *N*-soln. of **sodium chloride** are indicated in Fig. 67; the boundaries of the different solid soln. are indicated by dotted lines; the upper curve shows the variations in the amount of corrosion, and the lower curve represents grams of copper in the corrosion product. The curve for the γ-field is interpolated.

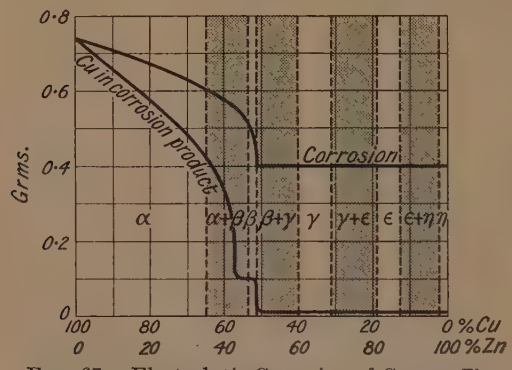

FIG. 67.—Electrolytic Corrosion of Copper-Zinc Alloys by Solutions of Sodium Chloride.

A. T. Lincoln, and G. C. Bartells found that the corrosion with synthetic **sea-water** is practically the same as with aq. soln. of sodium chloride. W. A. Tilden found that brass may be boiled with a soln. of sodium chloride for any length of time, without alteration, provided air is entirely excluded, and the attack by sea-water on ship's sheathing is generally worse near the water-line. M. Berthelot stated that with dil. soln. of alkali chlorides exposed to air, cuprous oxide and atacamite are formed, and zinc dissolved. The reports of the action of sea-water are not always concordant. A. Bobierre found that the zinc appears to be dissolved, and an oxidation product of copper formed. W. A. Tilden found that brass with 60 per cent. of copper is less attacked by sea-water and soln. of chlorides than is copper; corrosion pits are produced with brass in contact with other metals. Other observations were made by O. Silberrad, L. Belladen, R. Finkener, H. S. Rawdon, F. C. Calvert and R. Johnson, M. Diegel, etc. According to the last-named, the destructive action of sea-water on copper alloys rich in zinc is traceable to the destruction of the alloy by the extraction of zinc. When two metals are in contact in sea-water a voltaic current is set up, the metal being especially attacked which stands highest in the electromotive series—in the case of copper alloys, therefore

those richest in zinc. As a rule, the greater the difference in the electromotive order between the alloy and the metal in contact with it, the greater is the corrosion. According to P. de Wurstemberger, the mode in which brass is dezincified in contact with sea-water varies according to whether the brass contains only one phase, whether all α or all β, or both. In the first case the metal becomes gradually more or less uniformly coated with spongy copper, in the second case the β constituent is attacked first, and the metal has the appearance of a network of channels surrounding the α-grains. The primary cause of dezincification appears to be the deposition of a film of metallic copper on the surface of the metal from a salt or oxide of copper formed by the action of the salt water on the brass, and this gives rise to a concentration of copper ions sufficient to hinder polarization, the zinc then dissolves by electrolytic action. Selective corrosion is due to electrolytic action of stray or local currents, whereas dezincification may be considered to be due to selective corrosion that is still going on or has already stopped. The former phenomenon is characterized by the appearance of gelatinous deposits of an oxychloride of zinc along the α-crystal boundaries, and the water in contact with the metal reacts alkaline, whereas the latter is accompanied by deposition of spongy copper. O. Lasche discussed corrosion due to stray currents and local corrosion. R. B. Abrams studied the dezincification of brass.

W. A. Tilden found sodium chloride soln. attack brass faster than those of **magnesium chloride.** A. Wagner found that in the presence of air free from carbon dioxide, brass with 65 per cent. of copper, is but little attacked by soln. of magnesium or **potassium chloride,** with **ammonium chloride** there is strong corrosion; with air containing carbon dioxide, the action of ammonium chloride is reduced about one-half, and that with magnesium and potassium chloride soln. is augmented about 21 times. T. J. Baker noted that brass dissolves rapidly, with the development of gas, in a mixed soln. of **ferric and ammonium chlorides;** and in one of **cupric and ammonium chlorides.** According to H. P. Pearson, an alkaline soln. of **sodium hypochlorite** attacks copper-zinc alloys, slowly forming a dull green deposit, but no trace of either metal passes into soln.

According to T. G. Bamford and W. E. Ballard, brass at 300° absorbs **sulphur dioxide,** and the gas is eliminated from the metal between 950° and 1050° under reduced press. A. Wagner found that an alloy with 64·5 per cent. copper is not appreciably attacked by a soln. of **potassium sulphate** exposed to air free from carbon dioxide. A. T. Lincoln, D. Klein, and P. E. Howe observed the anodic corrosion of zinc-copper alloys by a *N*-soln. of **sodium sulphate.** The amount of corrosion is practically the same with all the alloys. N. A. Puschin found alloys with 0 to 14 at. per cent. of copper are feebly attacked by *N*-soln. of **zinc sulphate** at ordinary temp. J. Girard observed that 10 per cent. soln. of **sodium thiosulphate** attack brass a little, at 60°–65°. A. T. Lincoln, D. Klein, and P. E. Howe measured the action of *N*-soln. of **sodium persulphate** in alkaline soln. The alloys with 73·4 to 93·6 per cent. of copper were badly corroded on the test-pieces exposed to air; the 22·6 per cent. copper alloy was coated with a layer of copper owing to the removal of the zinc; the 3·1 to 10·5 per cent. copper alloy was coated with a black deposit; while the 60·3 to 76·3 per cent. copper alloy remained practically unchanged. With aq. soln. of sodium persulphate, the brasses of high copper content were badly corroded, the alloys with 51·3 to 3·1 per cent. of copper were coated with a film of copper. A. Wagner found that in the presence of air, and the absence of carbon dioxide, a soln. of **potassium nitrate** exerts no action on brass with 65 per cent. of copper; but if carbon dioxide be present there is a slight action. A. T. Lincoln, D. Klein, and P. E. Howe studied the action of a *N*-soln. of **sodium nitrate** and of **ammonium nitrate** on an anode of zinc-copper alloys. The corrosion products contained varying proportions of zinc and cupric hydroxides. With sodium nitrate, there is a gradual increase in corrosion as the amount of copper decreases until the $\beta+\gamma$ area is reached, while in the $\gamma+\epsilon$ area the alloy is less corroded, and as the proportion of copper decreases, the amount of corrosion increases in a marked

degree. Similar results were obtained with soln. of ammonium nitrate. A. Wagner found that a soln. of **sodium carbonate** does not attack brass when exposed to air free from carbon dioxide ; and the attack by a soln. of **potassium carbonate** in the presence of air with carbon dioxide is feeble. A. T. Lincoln, D. Klein, and P. E. Howe found that the anodic corrosion of copper-zinc alloys by *N*-soln. of sodium carbonate is feeble—white adherent coatings were formed on alloys with 3·1 to 10·5 per cent. of copper ; the alloys with 47·6–51·3 per cent. of copper were covered with a green film, and those with more copper were slightly discoloured. They also studied the anodic corrosion of zinc-copper alloys in *N*-soln. of **ammonium oxalate ;** those alloys with less than 47·6 per cent. of copper developed insulating films ; with the other alloys, the amount of corrosion increased with decreasing content of copper, making a maximum in brasses with $\alpha+\beta$-crystals, and then decreasing rapidly with the appearance of the γ-crystals. In the anodic corrosion in *N*-soln. of **sodium acetate,** the amount of corrosion increases rapidly with decreasing copper content, attains a maximum in the $\alpha+\beta$-region, and diminishes with the appearance of the γ-crystals. W. H. Walenn noted the solvent action of a soln. of **potassium cyanide** mixed with ammonium tartrate, and J. J. Hesz of a mixed soln. of potassium cyanide, sodium hydrocarbonate, and ammonium chloride.

According to C. J. B. Karsten, alloys with over 50 per cent. of copper exhibit the reactions of copper towards **acids,** but alloys with less than 50 per cent. of copper dissolve completely in acids which have scarcely any action on copper alone, and this the more rapidly, the greater the proportion of zinc. If the quantity of acid be not sufficient to dissolve the whole of the alloy, copper is reprecipitated until all the zinc is dissolved. J. J. Berzelius noted that brass becomes red when rubbed with hydrochloric acid, because the zinc dissolves in preference to the copper. O. Sackur, P. Maus, and A. Siemens found that there are breaks in the acid solubility curve of alloys with about 45 and 62 per cent. of copper ; alloys with less than 45 per cent. of copper do not yield copper to $\frac{1}{20}N$-**sulphuric acid,** but those with over 62 per cent. of copper yield copper as well as zinc to the dil. acid. H. Behrens found that the annealed alloy dissolves more readily in acid and salt soln. than the cast alloy. F. C. Calvert and R. Johnson found that sulphuric acid, at 150°, dissolves only zinc from alloys with an excess of zinc, and both copper and zinc are dissolved from alloys with an excess of copper ; $H_2SO_4.2H_2O$, at 150°, acts feebly on copper-zinc alloys, and not at all on that corresponding with CuZn ; A. Matthiessen, J. Laubheimer, H. Behrens, and O. Haug have also made observations on this subject. R. C. Griffin found the solvent action of sulphuric acid is lessened by formaldehyde. E. Harbeck found that a brass anode is not attacked by sulphuric acid of sp. gr. 1·53. F. C. Calvert and R. Johnson found **nitric acid,** sp. gr. 1·14, dissolves approximately equi-atomic proportions of the two metals from CuZn, and an acid of sp. gr. 1·08 approximately 5 atomic proportions of zinc for one of copper. Nitric acid of sp. gr. 1·1 acts but little on alloys with an excess of copper, and readily on alloys with an excess of zinc. R. C. Griffin found that formaldehyde slows down the attack with nitric acid. B. C. Banerji and N. R. Dhar found the presence of ferric chloride or nitrate, or ferrous sulphate accelerates the action of nitric acid on brass, while the presence of manganese sulphate, potassium chlorate, or potassium permanganate retards the action. F. C. Calvert and R. Johnson found that conc. **hydrochloric acid** dissolves zinc completely from the alloy with equi-atomic proportions of the two metals ; an acid of sp. gr. 1·05 does not act on this alloy or on alloys richer in copper, but it removes the zinc from alloys with a smaller proportion of copper, and this the more rapidly the greater the proportion of zinc. T. Schwarz found that **acetic acid** and **lactic acid** dissolve copper from brass ; A. Gawlowsky, that 4 per cent. acetic acid readily attacks brass ; and E. J. Paessler, that **fatty acids** attack brass.

J. J. Berzelius noted that brass becomes white if rubbed with aq. **ammonia** owing to the dissolution of the copper and not the zinc. J. Y. McLellan reported that if a piece of brass or brass turnings be covered with aq. ammonia, sp. gr. 0·880,

and confined in a stoppered bottle, a violet soln. will be produced in a few days owing to the dissolution of copper from the brass. H. Behrens found the attack of aq. ammonia is greatest on alloys with a moderate proportion of copper. W. Venator found a soln. of **sodium hydroxide** attacks brass slightly dissolving only the zinc; while G. Charpy found that a soln. of **potassium hydroxide** rapidly attacks copper-zinc alloys rich in zinc, and dissolves only the zinc, while alloys with about 25 per cent. of copper are attacked more slowly, because, he said, of the presence of Zn_4Cu. H. Behrens found that if the alkali lye contains some cupric tartrate, it attacks these alloys more strongly than does aq. ammonia. A. Wagner found a soln. of **calcium hydroxide** behaves like sodium hydroxide towards brass. J. J. Redwood found that the percentage loss when brass is treated with **mineral oil** is 0·2455; with **tallow oil,** 0·04929; with **lard oil,** 0·08860; with **sperm oil,** 0·02743; with **whale oil,** 0·02547; and with **seal oil,** 0·00951. A bright green coloration was produced with **olive oil.** A. Gawlowsky found that **rape seed oil** attacks brass strongly, raw **petroleum** very little, and **wort** not at all.

C. J. B. Karsten showed that alloys of zinc with over 50 per cent. of copper do not precipitate copper from soln. of its salts, but if less than this proportion of copper is present, the alloy decomposes the cupric salt at the expense of the contained zinc. O. Sackur, P. Maus, and A. Siemens found that alloys with 0 to 41 per cent. of copper precipitate copper from soln. of its salts; alloys with 45 to 60 per cent. of copper do not precipitate that element from soln. of cupric cyanide or thiocyanate; and alloys with over 62 per cent. of copper do not precipitate copper from ammoniacal soln. of the halides. The curve showing the activity of the copper-zinc alloys in this connection has breaks with 41–45 and 60–62 per cent. of copper. M. Herschkowitsch and H. Behrens, and G. Tammann have made observations on this subject.

A. F. Gehlen [23] noted that silver and zinc readily unite when fused in the respective proportions 1 : 2, forming a fine-grained malleable alloy with a tinge less blue than that of zinc. C. R. A. Wright showed that the two metals are miscible in all proportions when in the fluid state. N. W. Fischer also observed that an alloy of the two elements is obtained when a soln. of silver nitrate is precipitated with zinc. F. Mylius and O. Fromm made a similar observation. According to N. A. Puschin and M. Maksimenko, silver dissolves in small quantities in solid zinc, and silver dissolves up to 30 at. per cent. of zinc. The f.p. curve has been studied by H. Gautier, G. J. Petrenko, C. T. Heycock and F. H. Neville, H. C. H. Carpenter. According to G. J. Petrenko, there is a maximum at 710° corresponding with **silver zincide,** Ag_3Zn_2; the compound AgZn appears to be formed at 690°; Ag_2Zn_3, at 670°; and Ag_2Zn_5, at 636°; but there are differences of opinion as to the compounds which are formed; N. A. Puschin and M. Maksimenko give AgZn, Ag_2Zn_3, $AgZn_4$, and $AgZn_6$. G. J. Petrenko assumed that when the mixed crystals of ZnAg and Ag_3Zn_2 are slowly cooled, they break up into mixed crystals with 21·7 per cent. of zinc, and β-ZnAg; the latter at 266° develops heat and forms crystals of α-ZnAg. H. C. H. Carpenter and W. Whiteley's analysis of the system is shown in Fig. 68, and it shows that with 0 to 60 at. per cent., the diagram closely resembles that of the copper-zinc system for the same conc. There are six phases: (i) α-phase is stable at ordinary temp., and ranges between 100 and 62·7 at. per cent. of silver; (ii) β-phase exists only above 264°, for on cooling there is a eutectoidal inversion to $\alpha+\gamma$; (iii) γ-phase between 40 and 37·3 at. per cent. of silver, and is stable at ordinary temp.—with 40 at. per cent., this is silver zincide Ag_2Zn_3; (iv) δ-phase, with between 29 and 14·3 at. per cent. of silver, is stable at ordinary temp.; (v) ϵ-phase exists only above 300° approximately; and (vi) η-phase, with between 0 and 1 at. per cent. of silver, is stable at ordinary temp. There is some indecisive evidence of the existence of a compound Ag_2Zn_5. K. Bornemann found the compound Ag_2Zn_5 can exist at ordinary temp., and R. Kremann and F. Hofmeier say that it is the colour of nickel.

According to N. A. Puschin, the colour of alloys with from 0 to 30 at. per cent. of silver is indistinguishable from that of zinc, and they have a well-defined crystalline structure and coarse-grained fracture; alloys with 39 at. per cent. of silver

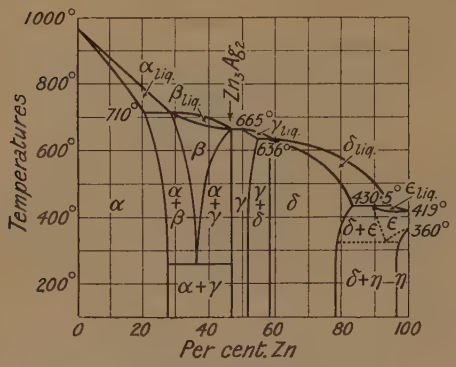

Fig. 68.—Fusion Curves of Zinc-Silver Alloys.

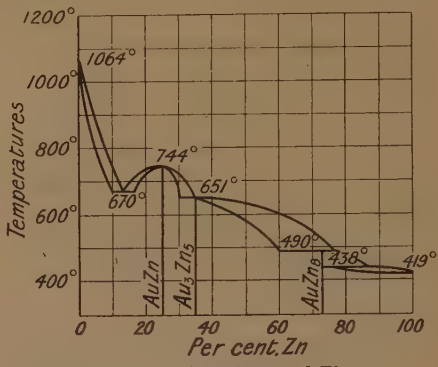

Fig. 69.—Fusion Curve of Zinc-Gold Alloys.

are white with a conchoidal fracture; alloys with 50 at. per cent. of silver are rose-coloured; and those with 63 per cent. of silver are pale yellow. C. T. Heycock and F. H. Neville, G. J. Petrenko, G. Charpy, H. C. H. Carpenter, and others have studied the minute structure of the alloys. E. Maey found a break in the sp. gr. curve for 80 at. per cent. of zinc. G. J. Petrenko found a maximum in the hardness curve between 47·61 and 60 per cent. of zinc; and N. A. Puschin obtained a maximum hardness with 33 and a second maximum with 50 at. per cent. of silver. C. T. Heycock and F. H. Neville, and E. M. Péligot studied the tensile strength of these alloys; and E. C. Bain, the X-radiograms; C. Barus and V. Strouhal measured the electrical conductivity; N. A. Puschin, the electrical resistance, the electrical conductivity, the temp. coeff. of the resistance, and the thermal e.m.f. M. Herschkowitsch found a break in the potential curve of alloys against zinc in N-$ZnSO_4$ soln. with alloys containing 80 at. per cent. of zinc corresponding with $AgZn_2$. R. Kremann and F. Hofmeier measured the e.m.f. of the cell Zn | N-$ZnSO_4$ | Ag—Zn alloy. E. M. Péligot studied the action of hydrogen sulphide and alkali sulphides on these alloys; and C. Montemartini and E. Colonna, the formation of ammonia when these alloys are dissolved in nitric acid. C. R. Groves and T. Turner observed that zinc is volatilized when these alloys are heated in vacuo below 1000°, and some silver also if over 1000°. D. Palitsch said that an alloy with 7 to 10 per cent. of silver dissolves in hydrochloric acid, forming a residue of allotropic silver. E. Sedström measured the Peltier effect with zinc-silver alloys. G. Tammann studied the difference in the potentials of alloys prepared by electrodeposition and by fusion.

Alloys of gold and zinc were early prepared by A. F. Gehlen,[24] J. Hellot, and C. Hatchett. The f.p. curve has been studied by C. T. Heycock and F. H. Neville, N. A. Puschin, C. H. Desch, and R. Vogel. The results are shown in Fig. 69. R. Vogel interprets the diagram by assuming that the **gold zincide,** AuZn, is represented by a maximum on the f.p. curve at 744°, and Au_3Zn_5 appears to be formed at 651°, and $AuZn_3$ at 490°. There is a eutectic at 648°. The colour of the gold zinc alloys changes from a pale yellow to a fine reddish-lilac tint as the proportion of zinc changes from 14 to 25 per cent.; with further additions of zinc, the colour gradually fades, and alloys with 25 to 30 per cent. of zinc consist of a white matrix with lilac-coloured polygonal crystals of AuZn. E. Matthey studied the homogeneity of the alloys. The microstructure was investigated by R. Vogel, and W. C. Roberts-Austen and F. Osmond; the sp. gr., by C. Hatchett; the hardness, by R. Vogel; the tensile strength, by W. C. Roberts-Austen; and the e.m.f. of

the cell Zn | $\frac{1}{2}N$-$ZnSO_4$ | Au—Zn alloy, by N. A. Puschin, who inferred the existence of the compounds $AuZn_6$, $AuZn_2$, and AuZn. C. R. Groves and T. Turner found that if the alloys with a low proportion of gold be heated 30–90 mins. in vacuo at 500°, the composition of the residue corresponds approximately with AuZn; if zinc cuttings be heated with sodium hydroxide in a gold crucible to 420°, the crucible is spoilt. E. Sedström measured the Peltier effect with gold-zinc alloys. G. Tammann studied the chemical activity of the alloy.

F. Stromeyer [25] prepared an alloy of cadmium and copper by melting the two elements together; C. R. A. Wright found that when melted, the two elements are miscible in all proportions; and P. Denso found that copper dissolves immediately in melted cadmium. F. M. Raoult found an alloy is produced when copper foil in contact with a piece of cadmium wire is dipped in a conc. soln. of cadmium sulphate. J. B. Senderens obtained an alloy by placing soln. of cupric sulphate, chloride, or acetate in a cadmium vessel. The f.p. curve of the two elements has been studied by R. Sahmen, C. T. Heycock and F. H. Neville, G. D. Roos, and H. le Chatelier. The results of the first-named are illustrated by Fig. 70. There are two eutectics corresponding respectively with 59·5 per cent. of cadmium at 542°, and with 98·84 per cent. of cadmium at 314°. The maximum corresponds with **cupric**

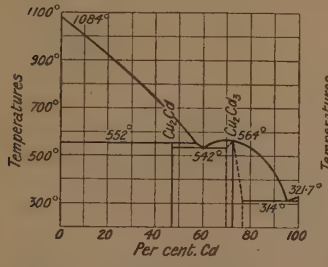

Fig. 70.—Fusion Curve of Copper-Cadmium Alloys.

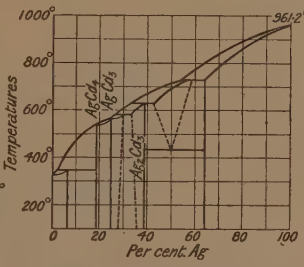

Fig. 71.—Fusion Curve of Silver-Cadmium Alloys.

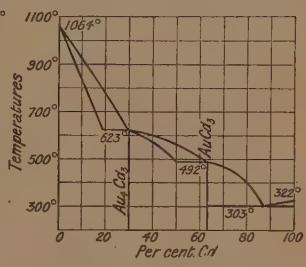

Fig. 72.—Fusion Curve of Gold-Cadmium Alloys.

cadmide, Cu_2Cd_3, melting at 564°, and with a heat of formation, according to W. D. Roos, of 47·7 ± 5·2 Cals. per mol, and a heat of fusion of 26·05 Cals. per mol. There is an abrupt change in the direction of the curve between 552° and 542°, with mixtures with between 56·5 and 59·5 per cent. of cadmium, and the solid alloys contain needle-like crystals of the cupride Cu_2Cd. F. Mylius and O. Fromm remarked on the greater sp. gr. of the compound Cu_2Cd than that of the separate constituents, and added that hydrogen is evolved by conc. hydrochloric acid, the copper is dissolved, forming cuprous chloride. P. Denso described the cupride $CuCd_3$ formed by crystallization from alloys with 1 to 10 per cent. of copper. The m.p. is above the vaporization temp. of cadmium. The faculty of copper to form solid soln. with cadmium, said N. A. Puschin, is feebler than with zinc. According to N. A. Puschin, alloys with less than 60 at. per cent. of copper are whitish, those with 68 per cent. are pale yellow, those with 75 per cent. are yellow, 80 per cent. rose, and 90 per cent. copper-red. R. Sahmen described the fracture; P. Denso, and R. Sahmen, the minute structure; G. Tammann and K. Dahl, the gliding planes at diff. temp.; W. Biltz and C. Haase, and E. Maey, the sp. gr., that of Cu_2Cd_3 being 9·35 at 25°/4°; W. Biltz and C. Haase, the heat of formation, *viz.*, —1·3 Cals.; N. A. Puschin, the hardness; and L. Guillet, G. Chaudoir, and F. Stromeyer, the tensile strength. W. C. Smith studied the mechanical and electrical properties of these alloys. E. Bornemann and K. Wagenmann found the electrical conductivity curve of the liquid alloys has a minimum corresponding with Cu_2Cd_3, making it possible that this cupride exists in the molten metal. G. Tammann studied the difference in the potentials of cadmium-copper alloys prepared by electrodeposition, and by fusion.

B. Wood [26] prepared a malleable, hard, and tough alloy of silver and cadmium

in the proportions 2 : 1, and found that the alloy 1 : 2 was brittle. J. B. Senderens made an alloy corresponding with $AgCd_3$, and F. Mylius and O. Fromm observed that an alloy of the two metals is formed by the action of cadmium on a soln. of silver nitrate. C. R. A. Wright found that the molten metals are mutually soluble in all proportions. According to C. T. Heycock and F. H. Neville, the m.p. of cadmium is raised, not lowered, by the addition of silver. T. K. Rose explained the complex f.p. diagram by assuming that the following **cadmium argentides,** $AgCd_3$, Ag_2Cd_3, AgCd, Ag_3Cd_2, Ag_2Cd, and Ag_3Cd, are formed, and G. Bruni and E. Quercigh assumed the existence of AgCd and $AgCd_4$. T. K. Rose commented on the analogy between Ag_2Cd_3 and Ag_2Zn_3, and between AgCd and AgZn. It is also stated that the two latter undergo allotropic changes below their m.p. E. Maey got a break in the sp. gr. curve corresponding with $AgCd_3$. The f.p. curve has been studied by H. Gautier, T. K. Rose, G. Bruni and E. Quercigh, and G. J. Petrenko and E. S. Federoff. A summary of the results is indicated in Fig. 71. H. C. H. Carpenter emphasized the close relationships between the copper-zinc, silver-zinc, and such portions of the silver-cadmium equilibrium diagram as are known ; and he suggests that in each system it is the compound X_2Y_3—where X represents Cu or Ag, and Y, Zn or Cd—which determines the character of the α- and β-phases, between 0 and 60 at. per cent. of zinc or cadmium. Otherwise, there is no eutectic in the silver-cadmium diagram, and solid soln. are formed throughout the series. R. Kremann and H. Ruderer measured the e.m.f., and E. Sedström, the Peltier effect of silver-cadmium alloys. G. Tammann studied the potential of alloys prepared by electrodeposition and by fusion ; and N. S. Kurnakoff and A. N. Achnasaroff, the effect of the velocity of cooling on the hardness and microstructure. E. Schreiner and co-workers measured the e.m.f. of silver-cadmium alloys. E. C. Bain studied the X-radiograms.

C. T. Heycock and F. H. Neville [27] made alloys of gold and cadmium, and studied their fusion points. F. Mylius and O. Fromm made alloys of these two metals by the action of cadmium on a soln. of auric chloride. According to P. Saldau, solid gold can dissolve up to 30 at. per cent. of cadmium, but solid cadmium only up to 2 at. per cent. of gold. R. Vogel, and P. Saldau have constructed equilibrium diagrams, Fig. 72. There is evidence of the formation of **cadmium auride,** Au_4Cd_3, at 625° : and of $AuCd_3$ at 495°, with a eutectic at 303° and 87 per cent. ; and of $AuCd_3$ at 495°, with a eutectic at 303° and 87 per cent. of cadmium. A maximum in the curve corresponds with the compound AuCd. The two compounds AuCd and $AuCd_3$ are represented by cusps in the electrical conductivity curves. The hardness has been measured by P. Saldau, and by R. Vogel ; there are maxima with 18 to 30 per cent. and 51 to 63 per cent. of cadmium. P. Saldai measured the e.m.f. of the cell Cd | N-$CdSO_4$ | Cd—Au alloy. He also found that the compound Au_4Cd_3 marks the limit of solid soln. in unannealed specimens and is not a real compound. W. C. Roberts-Austen measured the tensile strength of the alloys, and W. C. Roberts-Austen and F. Osmond, and R. Vogel studied the minute structure. Gold or silver alloyed with either cadmium or zinc can be parted with nitric or sulphuric acid. E. Sedström measured the Peltier effect with gold-cadmium alloys. G. Tammann studied the chemical activity of the alloy.

Alloys of copper and calcium have been prepared by L. Hackspill [28] by reducing cupric chloride with calcium at a red heat in vacuo ; and he stated that the two metals are mutually soluble in all proportions. The alloys are orange-yellow, brittle, and have a crystalline fracture ; they oxidize readily in air, and decompose water. L. Donsky found that one per cent. of calcium depresses the m.p. of copper 8°, and 5 per cent. lowers it 74°. N. Baar found what seems to be a eutectic at about 910° ; with 5·7 per cent. of calcium, and one at 560° with 38 per cent. of calcium. There is also evidence of the formation of one **calcium cupride,** Cu_4Ca, as shown by the f.p. curve, Fig. 73. A thermal change unaccompanied by a change of structure occurs at 480° in all alloys containing $CaCu_4$; these alloys are all white,

and unstable in air. Alloys with over one per cent. of calcium decompose cold water with the evolution of hydrogen. L. Hackspill prepared homogeneous alloys of silver and calcium by reducing silver chloride with calcium at a dull red heat in vacuo. The alloys are grey, and brittle, and have a crystalline fracture; they oxidize readily in air, and are decomposed by cold water. G. Tammann studied the chemical activity of the alloy. C. Vickers tried the effect of calcium, barium, and strontium as deoxidizers, etc., on copper.

N. Baar studied the f.p. curve of calcium and silver, and found evidence of the formation of the **calcium argentides**: Ag_4Ca, Ag_3Ca, Ag_2Ca, and $AgCa_2$—the latter is more or less doubtful. The f.p. curves shown in Fig. 74, are somewhat

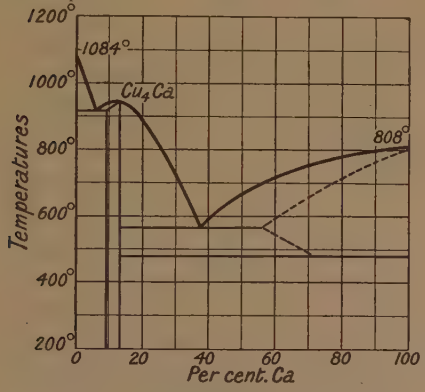

Fig. 73.—Fusion Curve of Copper-Calcium Alloys.

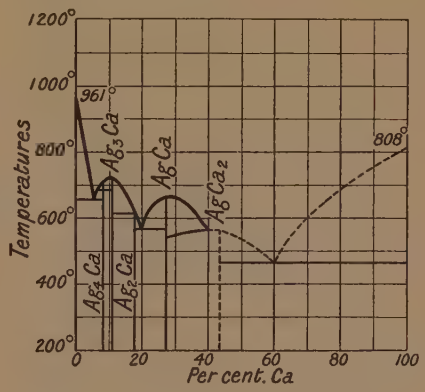

Fig. 74.—Fusion Curve of Silver-Calcium Alloys.

complex. The compounds Ag_3Ca_2 and AgCa being marked by maxima in the f.p. curve at 726° and 665° respectively, whilst the compounds Ag_4Ca, Ag_2Ca, and possibly $AgCa_2$, are formed at 683°, 595°, and 555° respectively. Solid soln. containing AgCa and $AgCa_2$ undergo a transformation at a lower temp. All the alloys containing more than 11 per cent. Ca decompose water. G. Tammann studied the chemical activity of the alloys.

L. Donsky found the f.p. curve of calcium and magnesium alloys to be of the simple W-type, Fig. 75. One compound, **calcium magneside**, Ca_3Mg_4, is formed with a maximum at 715°, and eutectics at 514° and 446° with respectively 18·7 and 78·7 per cent. of calcium. Solid soln. are not formed to any appreciable extent. The magneside Ca_3Mg_4 is brittle, and silvery in appearance; W. Biltz and G. Hohorst gave 1·701 for the sp. gr. at 25°/4°; and 127·9 for the mol. vol. L. Donsky found that it is stable in air, and but slowly acted on by water. The alloys of zinc and calcium were studied by H. Caron, G. vom Rath, T. H. Norton and E. Twitchell, H. Moissan, and L. Donsky. F. von Kügelgen and E. O. Seward prepared them by the electrolysis of molten calcium chloride with a zinc cathode. W. Moldenhauer and J. Andersen made alloys of zinc and calcium by the electrolysis of a molten mixture of calcium chloride with 15 per cent. of potassium chloride in an iron crucible containing some molten zinc which served as cathode; a graphite rod was used as anode. L. Donsky found that the f.p. curve of alloys of zinc and calcium has two maxima, Fig. 76, at 717° and 5·7 per cent. calcium and 688° and 28 per cent. of calcium, corresponding with the **calcium zincides**, $CaZn_{10}$ and Ca_2Zn_3 respectively, a break at 680° and 12·8 per cent. calcium, corresponding with the compound $CaZn_4$, which possibly melts without decomposition, and two eutectic points at 635° and 17 per cent. and 410° and 57 per cent. of calcium respectively. Between 29 per cent. and 56 per cent. of calcium, the compound Ca_2Zn_3 reacts with the fused mass at 431° to form a fourth compound, the composition of which could not be accurately determined, but may be CaZn. At 385°,

between 52 per cent. and 84 per cent. of calcium, a fifth compound, Ca_4Zn, is produced by reaction of the compound of unknown composition with calcium. Alloys containing up to 6 per cent. of calcium are rather harder than zinc, and are

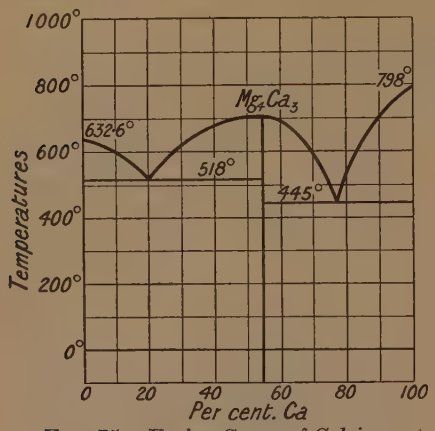

FIG. 75.—Fusion Curve of Calcium-Magnesium Alloys.

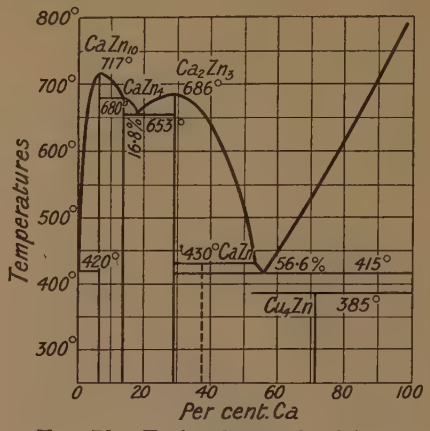

FIG. 76.—Fusion Curve of Calcium-Zinc Alloys.

fairly stable in air and towards water, but with increasing proportion of calcium they darken in the air and act more vigorously on water. The brittleness increases up to 30 per cent. of calcium, and then diminishes. G. D. Roos gave 76·95 Cals. per gram for the heat of fusion of $CaZn_{10}$; and 83·5 Cals. for $CaZn_4$; he also gave 199 Cals. per mol for the heat of formation of $CaZn_{10}$, and 55·6 Cals. for $CaZn_4$. W. Jenge, and G. Tammann studied the chemical activity of the alloy. H. Gautier made an alloy of strontium and zinc by the action of sodium on a fused mixture of zinc and strontium chlorides in an iron crucible at a red heat; or better, by heating a mixture of zinc, sodium, and strontium iodide. When heated zinc and strontium volatilize together.

L. Donsky also found that the f.p. curve of cadmium and calcium alloys, Fig. 77, does not show normal maxima, but there are two eutectic points at 319° and 1 per cent. of calcium (components calcium and $CaCd_2$) and 415° and 71 per cent. calcium (components $CaCd_3$ and mixed crystals rich in calcium). With between 12 per cent. and 64 per cent. of calcium, the alloys form two layers which react at 685° with formation of the **calcium cadmide**, CaCd; the latter has a transition point at 635°. At 615°, the compound CaCd reacts with the fused mass rich in cadmium to form a second compound, $CaCd_3$. A further break in the cooling curve at 510° appears to indicate a reaction between CaCd and the fused mass to form a third compound, the formula of which may be Ca_2Cd_3. Alloys containing up to 10 per cent. of calcium are stable in the air, and scarcely act on water; beyond that point, the action on water increases with increase in the proportion of calcium. The brittleness increases rapidly between 10 per cent. and 40 per cent. of calcium, and beyond that point diminishes. W. Jenge, and G. Tammann studied the chemical activity of the alloy. H. Gautier made an

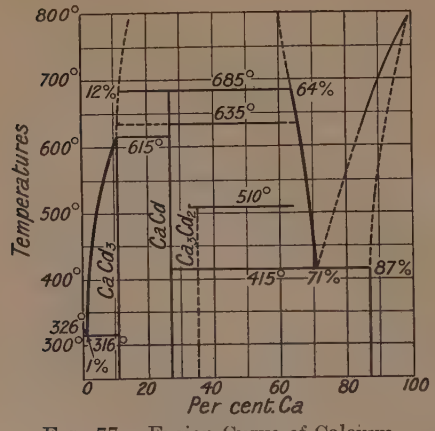

FIG. 77.—Fusion Curve of Calcium-Cadmium Alloys.

alloy of strontium and cadmium in a similar way to that employed for the strontium-zinc alloy. It was found to oxidize readily in air; to decompose water rapidly; to burn in oxygen or sulphur; and to form strontium hydride when heated in hydrogen, and strontium nitride when heated in nitrogen. It is attacked by chlorine, bromine, iodine, sulphur, and phosphorus. H. Gautier also made an alloy of barium and cadmium in a similar way. Its properties are similar to those of the strontium-cadmium alloy.

J. Parkinson [29] prepared an alloy of zinc and magnesium by melting the two elements together. Magnesium was found by C. T. Heycock and F. H. Neville to dissolve readily in molten zinc without any perceptible evolution of heat. O. Boudouard found that if an alloy with 20 per cent. magnesium be treated in the cold for some days with 0·003*N*-hydrochloric acid, pulverulent **magnesium dizincide,** $MgZn_2$, remains; while an alloy with 30 per cent. of magnesium when treated with 0·005*N*-ammonium chloride gives pulverulent $ZnMg_4$—rapidly when heated, slowly in the cold. C. A. Kraus measured the electrical conductivity of magnesium dizincide. G. Grube denied the existence of $ZnMg_4$ as a chemical individual. R. de Montgelas obtained an alloy of zinc and magnesium by the electrolyses of a conc. soln. of zinc and magnesium chlorides in the proportions 1 : 2; A. Siemens also investigated this subject. T. L. Phipson, and A. Roussin found that an acid soln. of a zinc salt gives a precipitate of zinc when treated with magnesium; and from a soln. of a neutral zinc salt, A. Commaille obtained a mixture of zinc, zinc hydroxide, and a basic zinc salt. H. N. Warren obtained a magnesium-zinc alloy by the action of zinc-sodium alloy on molten sodium magnesium chloride, or by the electrolysis of the same with a zinc electrode. G. Masing made an alloy of these elements by compressing a mixture of filings under 3000–5000 atm. press. The f.p. diagram, Fig. 78, has been investigated by G. Grube, G. Masing, O. Boudouard, and C. T. Heycock and F. H. Neville. The curve is the simple W-type, and O. Boudouard placed the maximum corresponding with Zn_2Mg at 570°, and G. Grube at 595°. A. J. Berry found that magnesium dizincide can be prepared by distilling the more volatile metal from a mixture of the two metals. The compound itself can be distilled in exhausted glass tubes at temp. lower than the softening point of glass. The lowering of the f.p. of zinc by magnesium was found by C. T. Heycock and F. H. Neville to be greater than with any other metal. The alloys are all white and more or less difficult to polish. The minute structure has been studied by O. Boudouard, and G. Grube. Alloys with 10 per cent. of zinc were said by O. Boudouard to be readily sawn or filed, and by G. Grube, to be malleable when hammered. As the proportion of zinc increases, the alloys become more brittle. G. Grube found most of the alloys to be brittle. The compound Zn_2Mg is not affected by water. J. Parkinson found that the alloys slowly lose their lustre in air. O. Boudouard etched the alloy with potassium hydroxide; C. Montemartini and E. Colonna studied the formation of ammonia when the alloy dissolves in nitric acid. H. Fleck obtained zinc and magnesium iodides and a little magnesium ethyl by treating the alloy with ethyl iodide. N. J. Stepanoff estimated 10·782 Cals. for the heat of formation of a mol of Zn_2Mg, and G. D. Roos estimated 25 Cals. per mol; for the heat of fusion, the last-named gave 65·8 Cals. per mol. H. von Wartenberg computed the heat of formation of $MgZn_2$ to be 1314 ± 180 cals.; and for the reaction $Mg_{gas}+2Zn_{gas}=MgZn_{2gas}+59$ Cals. G. D. Roos gave 24·5 cals.; and W. Biltz and G. Hohorst, 12·6 cals., 5·126 for the sp. gr. at 25°/4°, and 30·24 for the mol. vol. H. von Wartenberg found that the compound $MgZn_2$ distils unchanged at 600°,

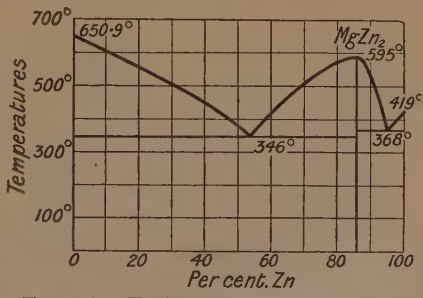

FIG. 78.—Fusion Curve of Magnesium-Zinc Alloys.

but it is completely dissociated at 1300°. If p_1 be the vap. press. of the magnesium ; p_2 that of the zinc ; and p that of the compound $MgZn_2$, $p_1p_2^2K=p_1$, and log K $=13000T^{-1}-3{\cdot}5 \log T+2$ (to 4). W. Jenge studied the electrical and chemical properties of the alloys of magnesium and zinc. According to E. Weinwurm, the alloy *electron* contains 80 per cent. of magnesium and 20 per cent. of other metals—mostly zinc. It easily oxidizes in air ; is dissolved by acid and salt soln. and tap water ; it is not attacked by soln. of caustic alkalies ; soln. of cellulose esters dissolve it ; it can be cast, forged, rolled, or drawn, and it machines easily ; it is a good conductor of electricity.

J. Parkinson prepared an alloy of cadmium and magnesium by melting the two metals together at a dull red heat in a hard glass tube in an atm. of hydrogen. G. Grube, R. Ruer, and O. Boudouard studied the f.p. curve. The latter obtained three maxima corresponding with the **magnesium cadmides,** CdMg (500°), CdMg (565°), and $CdMg_{30}$ (650°), and he claimed to have prepared the first two by the method employed for the corresponding compounds of zinc, Fig. 79. G. Grube reported that the f.p. curve of the system magnesium-cadmium falls continuously from the m.p. of magnesium to that of cadmium, but shows a slight break at 82·19 per cent. by weight of the latter metal, corresponding with the composition of the compound CdMg ; this substance forms a complete series of mixed crystals with both its components. When the cooling is rapid, the crystals separating between 20 and 95 per cent. of cadmium are not homogeneous, owing to equilibrium between the melted alloy and the crystals not being established with sufficient rapidity. There is no evidence of the existence of the compounds $CdMg_4$ and $CdMg_{30}$ mentioned by O. Boudouard. The compound CdMg is greyish-white and slightly harder than cadmium ; it becomes oxidized in moist air and is readily acted on by water. G. D. Roos gave 17·7 Cals. per mol for the heat of formation of MgCd, and he estimated that it undergoes association to the extent of 16 per cent. ; W. Biltz and G. Hohorst gave 9·2 cals. ; and 5·383 for the sp. gr. at 25°/4°, and 25·4 for the mol. vol. L. Guillet measured the hardness of these alloys. W. Jengo studied the electrical and chemical properties of magnesium-cadmium alloys ; and L. Aitcheson the mechanical properties.

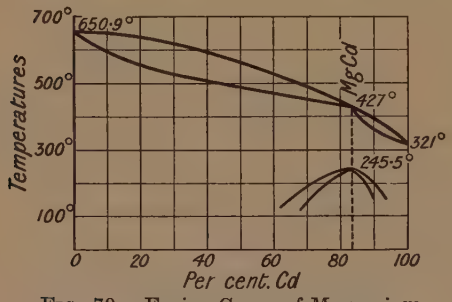

FIG. 79.—Fusion Curve of Magnesium-Cadmium Alloys.

Alloys of cadmium and zinc were prepared by B. Wood ; [30] and C. T. Heycock and F. H. Neville, and C. R. A. Wright found the two metals mix in all proportions, and G. Hindrichs found that although the molten metals are completely miscible, no compound and no mixed crystals are formed, but the two metals on solidification crystallize separately. E. Maey, H. Gautier, C. T. Heycock and F. H. Neville, N. A. Puschin, and B. E. Curry failed to obtain any sign of chemical combination. The f.p. curve of zinc and cadmium alloys is of the simple V-type. It was investigated by G. Hindrichs, H. Gautier, C. T. Heycock and F. H. Neville, and D. V. Plumbridge. The m.p. of zinc falls from 419° to the eutectic 270° when 82·6 per cent. of cadmium is present ; it then rises to 322°, the m.p. of cadmium. The minute structure was examined by most of these investigators. S. Lussana measured the compressibility of zinc-cadmium alloys. G. Masing found that the structure of the alloy obtained by compressing a mixture of finely divided zinc and cadmium between 1000 to 4000 atm. is quite different from that obtained by fusing the metals together. The sp. gr. was investigated by G. Vicentini and D. Omodei, E. Maey, and B. E. Curry ; the hardness, by A. V. Saposhnikoff and M. Sacharoff, and N. S. Kurnakoff and A. N. Achnasaroff ; the mechanical properties, by W. Voigt

and J. Miller, and O. Meyer; the coeff. of thermal expansion, by G. Vicentini and D. Omodei; the electrical conductivity, by A. Matthiessen, E. Rudolfi, W. Guertler, G. Tammann and K. Dahl, and G. Vicentini and C. Cattaneo; the potential in soln. of sodium chloride, by A. P. Laurie; the e.m.f. of the cell Zn | $ZnSO_4$ | Zn—Cd alloy, by N. A. Puschin; of Cd | $MgSO_4$ | Mg—Cd alloy, by R. Kremann and J. G. Pammer; and the thermo-e.m.f. against lead, by A. Battelli. C. Montemartini and E. Colonna studied the formation of ammonia during the dissolution of alloys of zinc and cadmium in dil. nitric acid. E. Jänecke studied the ternary system, Mg—Zn—Cd.

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CHAPTER XXXI

MERCURY

§ 1. The History and Occurrence of Mercury

MERCURY is not mentioned by Moses in the Pentateuch, nor by the earlier Greek writers, and H. Kopp,[1] therefore, inferred that the discovery of this element came later than that of gold, silver, copper, tin, lead, or iron. M. Berthelot believed that tin-amalgam and copper-amalgam were known to the ancient Egyptians under the name *asem*. According to S. Seligmann, the discovery by H. Schliemann of a small vessel full of mercury in a grave at Kurna, and estimated to belong to the sixteenth or fifteenth century B.C., shows that this element must have been known a very long time. A. Weiskopf was of the opinion that this element was probably known to the Phœnicians and Carthagenians 700 B.C. In his *Meteorology*, Aristotle, 320 B.C., mentioned mercury—*ἄργυρον χυτόν*, liquid silver—and stated that it must contain much water and air because it resists solidification by cold ; and in his *De anima*, Aristotle also referred to its use by the priests. A few years afterwards, Theophrastus, 300 B.C., in his *Περὶ Λίθων*, stated that *ἄργυρον χυτόν* is obtained by rubbing native cinnabar with vinegar in a copper mortar with a copper pestle. Discoveries of stone hammers, arrow-heads, wooden plates, and coins, made around Monte Amiata, Italy, show that these mines were worked for cinnabar by the Etruscans, and later by the Greeks and Romans. These relics are preserved in museums at Sisle and Cornacchino. About the beginning of the Christian era, Dioscorides, in his *De materia medica*, called mercury *ὑδράργυρος*—*ὕδωρ*, water ; *ἄργυρος*, silver—and stated that it is obtained by sublimation from cinnabar and charcoal in an alembic or iron pot with a luted *ἄμβιχ*, that is, a cap to collect the condensed vapour. Evidently, about this time mercury was well known to the Greeks and Romans. Near the beginning of the present era, Pliny, in his *Historia naturalis* spoke of *hydrargyrum* in contradistinction to *argentum vivum*, and, according to J. Beckmann, the first term probably referred to mercury separated from the ore by an artificial process, and the second term signified native mercury. Pliny stated that all substances other than gold float on the surface of the metal ; and he added that the mercury can be purified by squeezing it through leather, from which it "exudes like a kind of perspiration." About the same time, Vitruvius, in his *De architectura*, described the preparation of mercury from cinnabar, and, at the beginning of the seventh century, Isodorus, in his *Origines*, described some properties of the liquid.

Mercury played an important *rôle* in the work of the Alexandrian and later alchemists, inasmuch as it was regarded as one of the three primitive elements from which all matter was made ; and, in particular, they believed a substance resembling mercury, if not mercury itself, to be an essential part of all the metals, and it was sometimes called the mother of metals. Leonardo da Vinci, however, would have none of it, and, in his *Codex atlanticus*, said :

> The deceitful interpreters of nature assume mercury to be the common germ of all the metals, forgetting that nature varies its seeds according to the different things which those seeds are meant to bring forth.

According to B. Neumann, the term *mercurius* was first employed by the

alchemists in place of quicksilver. Up to the sixth century, when mercury was regarded as a kind of silver, *quicksilver*, it was represented by the moon-crescent ☽, but, according to M. Berthelot, about this time the symbol for the planet Mercury ☿ was used for quicksilver, and the symbol for Jupiter was reserved for tin—previously, the symbol ☿ was often used for tin. During the alchemical period, mercury was diligently studied, and numerous compounds were prepared and many of the properties were closely examined. Thus, the Latin Geber—in his *Summa perfectionis magisterii*—described the preparation and properties of purified mercury; Albertus Magnus—in his *Compositum de compositis*—synthesized cinnabar, mercuric sulphide; and Thomas Aquinas—in his *Secreta alchemiæ*—studied soln. of metals in mercury to which he applied the term *amalgams*. According to A. Libavius, amalgam is a corrupted form of μαλάγμα, but, according to J. Ruska, it is a corrupted form of Greek μῖγμα with the Arabic prefix *al*, making *almagma*.

G. Agricola regarded mercury as a metal, but others were puzzled by it. A. Libavius, and J. J. Becher classed it among substances—like bismuth, arsenic, sulphur, etc.—which have a relationship with the metals. J. Kunckel said that mercury contains a tough sticky material; H. Boerhaave, R. A. Vogel, and G. L. L. de Buffon emphasized the differences in the physical properties of mercury and those of the common metals; G. Brandt called it a half-metal. The truly metallic nature of mercury was recognized when J. A. Braun, in the winter of 1759–60, at St. Petersburg, found that it could be frozen to a solid metal by cooling with a freezing mixture of snow and nitric acid, and when A. L. Lavoisier showed its elementary nature. The history of mercury has been discussed by G. F. Hildebrandt, A. Rössing, F. X. M. Zippe, G. A. J. Lambert, E. O. von Lippmann, and R. Andrée.

The occurrence of mercury.—Mercury is neither abundantly nor widely distributed; it occurs native, in very subordinate quantities, disseminated in liquid globules or filiform masses in cinnabar deposits as a decomposition product of that mineral, and hence, generally near the outcrop. It rarely occurs in individual globules large enough to allow the mercury to be profitably collected, although considerable quantities have been found in various deposits in California. It has been reported—F. B. de Sauvage,[2] J. A. C. Chaptal, M. de Serres, and P. G. de Grouville—unaccompanied by cinnabar, in the weathered granite at Mélinot (St. Lo, France), and accompanied by calomel in the strata on which Montpellier (Hérault) stands. It also occurs in silvery-white cubic crystals alloyed with silver, as a native *amalgam*, at Moschel (Rhenish Bavaria), at Rosenau (Hungary), Allemont (Dauphiné, France), Arqueros (Coquimbo, Chili), Almaden (Spain). Analyses of the amalgam range from $AgHg_3$ to Ag_5Hg_3. There is also a variety named *arquerite* from Arqueros (Chili) which, according to I. Domeyko, has the composition Ag_6Hg. A specimen of native *gold amalgam*, from Columbia, analyzed by H. Schneider, had $(Au, Ag)_2Hg_5$; and one from California, analyzed by F. L. Sonnenschein, had Au_2Hg_3. W. Vernadsky, E. Halse, and G. Flink have studied the occurrence of the various amalgams, etc.

Mercury is usually obtained from locally concentrated deposits of mercuric sulphide—*cinnabar*, or *cinnabarite*—more or less intermixed with the metallic oxides, earths, bituminous matter, iron pyrites, arsenical or antimonical compounds, and ores of gold, copper, and zinc. Its geological distribution ranges from the oldest to the most recent. It is found as a secondary formation from eruptive rocks, and in deposits from sulphurous springs. Thus, A. Liversidge[3] reported mercury and mercuric sulphide in the deposits from the hot springs near Ohaiawai (New Zealand), and G. F. Becker and W. H. Melville in the sinter from Steamboat Springs (Nevada). J. A. Phillips, and J. le Conte and W. B. Rising have discussed the deposits now being formed in the fumaroles near Lake Clear (California). F. L. Ransome has investigated the deposits at Almaden; and E. Wittig, those of Mexico. Some cinnabar is coloured black—*hepatic cinnabar*—by a hydrocarbon called *idrialine*, C_3H_2, and is called *idrialite*; *coralline earth* is a mixture of cinnabar,

bituminous matter, and about 60 per cent. of apatite, or calcium phosphate.[4] *Metacinnabarite* is a dimorphous variety of mercuric sulphide, and a variety containing some zinc is called *leviglianite*.

The most important deposits of cinnabar in **Europe** are at Almaden (Spain), Idria (Carniola, Austria-Hungary), and Nikitowka (Bachmut, South Russia). The mines at Almaden, Greneda, and Oviedo were described by Theophrastus, 300 B.C.; they were mentioned by Pliny, and Vitruvius; and they are still the most important of those in Europe. The Almaden deposits lie on the upper Silurian shales, and the average ore yields 8–9 per cent. of mercury, while the richest ore runs as high as 25 per cent. of metal. The mercurial exhalations in the hot mines make the mining an unhealthy occupation. The Idria deposits have been worked since 1490; and from the old spoil heaps, it is supposed that the deposits at Nikitowka were worked in ancient times at an undetermined period, and it is estimated to be one of the most important deposits in the world. A deposit fourth in importance occurs at Monte Amiata (Italy). Other subordinate deposits occur at Vallalota near Agorda, Bagno S. Filippo, Saturnia, Fano Monte delle Fate, Causoli, Castiglione, Chiaverese, Albareto, Marguo, and San Donato di Ninea in Italy; in the Avala Hills of Serbia; Spizza, and Nehaj in Dalmatia; at Tristyn in Croatia; Mires, Santander, Tobiscon, and Purchena in Spain; Neumarktel, and Littai in Carniola; Balagna, and Capo Corso in Corsica; Isère, Haute Vienne, and Sevennes in France; Kongsberg in Norway; and Sala in Sweden. There are exhausted deposits at Wolfstein and Moschellandsberg in the Bavarian Palatinate; at Horrowitz in Bohemia; and at Volterra, Cerighani, and Ripa in Italy. In **Asia,** there is an extensive deposit in the provinces of Kweitshow, and Hoang Hai in China; Senday in Japan; Ildekansk in Siberia; in Borneo; Java; Sumatra; and near Smyrna. In **Africa,** there are deposits in Algeria and in Tunis. In **America,** the output from the deposits at New Almaden, New Idria, and other parts of California exceeds that of Almaden. Work was begun at New Almaden about 1851. The deposits of Almaden and Idria seem to get richer from above downwards, while those in California are said to get poorer. Cinnabar has also been reported and in some cases worked in Texas, and Oregon; in British Columbia; near Capula, St. Romualdo Pedemal, Carro, Dulces Nombres, Guadalupana, Guadalcazar, Huitzuco, and Zacatecas in Mexico; Huancavelica, Chonta, Cajamarca, and Santa Cruz in Peru; Andacallo in Chili; Tolima in Columbia; La Cruz and Santo Tomé in the Argentine; and at Paranagra, Santa Catherina, Santa Paulo, and Oro Preto in Brazil. The Huancavelica mines of Peru began to produce mercury in quantity about 1571. The mines at Guadalcazar in the province of San Luis Potosi (Mexico) were known to the "Indians" before the discovery of Mexico by Spain. In **Australasia,** cinnabar occurs at Cudgegong, and Noggringa Creek in New South Wales; at Kilkivan in Queensland; and at Omaperesee in New Zealand.

The world's production of mercury, in flasks of about 75 lbs., was:

1880	1890	1900	1906	1914	1917
119,168	101,656	99,240	108,120	107,589	122,092

The maximum and minimum prices per flask in 1916 were respectively £18 15*s.* and £16 12*s.* 6*d.*, and in 1919 respectively £24 10*s.* and £15 10*s.* The pre-war price was about £7 per flask. The production in flasks of about 75 lbs., in different countries, was:

	United States.	Spain.	Austria-Hungary.	Italy.	Russia.	Mexico, etc.
1906 . .	28,890	37,260	17,130	12,540	6,300	6,000
1914 . .	16,548	28,000	27,500	31,541	—	4,000
1917 . . .	35,954	25,133	27,500	29,300	500	4,000

The other minerals and ores of mercury are of no economic importance so far as the extraction of the element is concerned. There are the minerals: *tiemannite*, HgSe, which, according to G. F. Becker, was once commercially worked in Utah; *coloradite*, HgTe; *onofrite*, or *guadalcazite*, ZnS.6HgS; *lehrbachite*, or *lerbachite*, HgSe+PbSe; *calgoorlite*, $Ag_2Au_2HgTe_6$; *livingstonite*, $HgS.2Sb_2S_3$, or $FeS_2.HgS.4Sb_2S_3$; *montroydite*, HgO; *calomel*, or *horn quicksilver*, HgCl; *bordosite*, possibly AgCl.2HgCl; *coccinite*, HgI_2, is doubtful, it may be a mercuric chloroselenide; *terlinguaite*, Hg_2OCl; *eglestonite*, Hg_4OCl_2; *magnolite*, Hg_2TeO_4; *kleinite*, $3HgO.HgCl_2$ or $Hg_4[O(NH_2)_2]_3(\frac{1}{2}SO_4, Cl)_2$; and *mosesite*, which is similar to kleinite and is a mixture of ammonium mercurochloride with mercurous sulphate and possibly chloride; *barcenite* is supposed to be a mixture of calcium mercury antimonate and antimonic acid.

Mercurial earths at Guadalcazar are called *acerado*, and *fierroso*. There are *mercurial fahlores* containing some cinnabar—may be up to 18 per cent. Hg—also called *hermesite*, at Ober-Moschel; *schwatzite*, at Tyrol; and *spanoilite*. A. Kretschmer found 0·75 per cent. Hg in a sample from Müsen, 1·52 per cent. in one from Kotterbach, 0·80 in one from Brixlegg; and A. d'Achiardi, 3 per cent. in one from Zulfello (Tuscany).

F. Sandberger found mercury in copper; H. Wurtz reported 0·99 per cent. in *animicite*, Ag_6S_6; L. E. Rivot, 22 per cent. in a cupric antimonate with mercuric telluride from Chili; F. Field also found mercury in cupric antimonate; A. M. del Rio in zinc selenide; M. Barval reported mercury in Caucasian iron ore; H. Wurtz, 1·04 to 1·11 per cent. in *huntilite*; P. Collier found 1·30 per cent. of mercury in *stromeyerite* from Arizona; and A. Hilger found 15·79 per cent. of mercury as cinnabar mixed with a stibilite from Mexico. Many varieties of zinc blende have been reported to contain mercury—*e.g.* by E. Hairs in the blende from Bleyberg; F. L. Bartlett in the blende from Leadville; L. de Launay and G. Urbain in tertiary blendes; 0·02 per cent. in the Rhenish and Swedish blendes; and P. Soltsien, 0·135 per cent. in Asturian blendes.

The literature on the Californian ores has been collected by W. Forstner;[5] the Oregon deposits, by B. A. Wendeborn; the Arizona deposits, by F. C. Schrader; the British Columbia deposits, by G. F. Monckton; the Idria mines, by A. Schrauf; the Monte Amiata mines, Italy, by A. Verri, P. de Ferrari, B. Lotti, and V. Spirek; the Mount Avala mines of Serbia, by H. Fischer; the Almaden mines of Spain, by H. Kuss; the Huancavelica mines of Peru, by A. F. Umlauff; the deposits of Borneo, by F. Katzer; the Algerian deposits, by M. Dussert; and the principal deposits of the world by L. Demaret. General collections have been made by E. Detienne, E. Fuchs and L. de Launay, A. W. Stelzner and A. Bergeat, R. Beck, F. Beyschlag, P. Krusch and J. H. L. Vogt, and C. Hintze. G. F. Hildebrandt collected the earlier literature.

F. W. Clark thus describes G. F. Becker's views on the origin of mercury ores:

The chief deposits of mercurial ores are all in the neighbourhood of igneous rocks, from which it is highly probable they were originally derived. The deep-seated granites, in his opinion, form the principal source of the mercury. The ore bodies in some cases fill fissures, fractures, or cavities in rocks, the latter being commonly of a sedimentary character; and in other instances the cinnabar forms impregnations in sandstone or limestone. The ores are commonly associated with pyrite or marcasite, sulphur, calcite, barite, gypsum, opal, quartz, and other secondary minerals, and show distinct evidence that they have been brought up from below in soln. In many cases, if not in all, the evidence of hydrous or solfataric origin is very clear. In G. F. Becker's opinion alkaline soln. containing sulphides are the natural solvents of the mercurial compounds, although V. Spirek, describing the deposits at Monte Amiata, Tuscany, suggests that the mercury was first dissolved as sulphate and precipitated later by alkaline polysulphides. For this supposition there seems to be little or no positive evidence. At Idria, A. Schrauf found no indications of the existence of alkaline thermal springs.

C. de Watteville[6] claimed that the solar spectrum has no mercury lines, and the presence of that element in the sun is doubtful. J. N. Lockyer found mercury lines in the spectra of the cooler stars. J. L. Proust discussed the occurrence of mercury in the waters of the sea. G. F. Becker reported mercuric sulphide in some Californian waters, and F. Garrigou in the Rocher spring water at Saint Nectaire-le-Haut (Pay-de-Dôme), but J. Lefort and E. Willm doubted if mercury is a constant constituent of the Rocher spring. P. E. Raaschou reported mercury in some mineral waters. J. Bardet examined spectrographically the waters of 54 French springs, and found that mercury was rarely present. J. L. Proust, H. M. Rouelle, J. F. Westrumb, F. Wurzer, and J. Kunckel found mercury in sodium chloride, and in sea-water—the test was made by distilling the salt with sulphuric acid, and the latter may have contained mercury. M. Miropolsky found mercury in sulphuric acid; P. E. Raaschou, in copper; L. Houllevigue, in the carbon filaments of incandescent lamps; and E. Wollschlaeger, in *Codeinum phosphoricum*. G. Seyfriedsberger found mercury in the walls and masonry of a mercury kiln. The so-called mercurial soot, or in Almaden *hollines*, and in Idria *stupp*—from the Slavonic *stupa*, dust—is the flue-dust which collects in mercury extraction furnaces, and is in some respects analogous with zinc fume or blue zinc. Stupp consists of a mixture of finely-divided mercury, soot, mercuric oxide, sulphide and sulphate, quartz, etc. It is subsequently treated for the mercury it contains. A. F. G. A. Leymerie found mercury in the roots of the mulberry tree at Valleraugue; and L. Oelkers, in tape-worms from man after treatment with mercurial salve; E. Ludwig and E. Zillner

found very little mercury in the brain and bones, more in the spleen and liver, and still more in the kidneys, and in parts of the large intestine of a man poisoned with mercurial salts. H. Winternitz noted that mercury is partly removed from the system by the urine.

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§ 2. The Preparation and Extraction of Mercury

The early processes for the extraction of mercury have already been indicated. They were described by G. Agricola in 1556. In 1719, A. Jussieu [1] described the process of extraction employed at Almaden, and in 1776, B. G. Sage, the process of extraction employed in the Palatinate. In virtually all cases, cinnabar is the only ore from which the metal is extracted, and the simplicity of the reduction is such that extremely poor ores can be profitably worked ; the bulk of the mercury in commerce is obtained from ores containing 0·5 to 1·0 per cent. of metal ; indeed, in some places, an ore with 0·75 per cent. of mercury is considered to be comparatively rich. The ore is not concentrated by wet processes because cinnabar is so friable that a considerable proportion would be lost by floating off with the water. As a rule, the rich portions of the ore are separated at the mine by spalling, and hand-picking ; the poorer ores are classified by screens or trommels into coarse and fine. Each of these grades may be re-classified. The general result is (i) a " rich small ore " running about 6 per cent. of mercury and of a grain size up to 0·32 in. diam. ; (ii) a " medium small ore " up to about 1·2 ins. diam. with about 0·6 per cent. of mercury ; and (iii) a " poor coarse ore " with pieces between 1·2 and 4 ins. in diam., and running about 0·3 per cent. of mercury. The coarse ore is treated in shaft furnaces both in Europe and in America ; the medium ore is treated in shaft furnaces in America, and in shelf or cascade furnaces in Europe ; and the fine ore is treated in Europe in reverberatory furnaces. Rich ores are treated in retorts, as in America, or in tile furnaces, as in Europe. Formerly all the furnaces were intermittent, but continuous furnaces are now employed.

Two general methods are available on a large scale for the reduction of cinnabar. The one depends on the oxidation of heated cinnabar by air, mercury vapour, and sulphur dioxide being formed : $HgS+O_2=Hg+SO_2$; in the other the cinnabar is heated with lime in a vessel from which air is excluded, calcium sulphide and sulphate are formed, and mercury vapour is set free : $4HgS+4CaO=3CaS+CaSO_4+4Hg$; instead of lime, iron in the form of smithy-scales can be used : $HgS+Fe=FeS+Hg$. In every case the reactions take place at a temp. exceeding the b.p. of mercury, so that the condensation of the vapour is an essential part of the process. J. F. Booth showed that if the ore is very rich in sulphur, some sulphur vapour may pass on to the condensers and re-form mercuric sulphide. In the air oxidation, the vapour of mercury is largely diluted with sulphur dioxide, nitrogen, oxygen, and generally with the products of combustion ; under these conditions, as in the case of zinc, the mercury vapour condenses with difficulty, and more or less mercurial soot, hollines, or stupp is formed, and this requires special treatment in order to recover the mercury. Nevertheless, the condensation of mercury vapour, highly diluted with furnace gases, is more easily effected than is the case with zinc vapour under similar conditions, first because, when sufficiently cooled, mercury passes into the liquid state ; and on account of its high sp. gr. it can be separated without

great difficulty. The mercury vapour obtained when the cinnabar is heated with lime or iron in retorts is readily condensed, but under these conditions, only small quantities can be treated at a time, the retorts last for a comparatively short time, the costs of fuel and labour are high, and the workmen are exposed to mercurial fumes when the retorts are cleaned. In the air-oxidation process, the costs of fuel and labour are comparatively small, and the workmen are not troubled by mercurial fumes. The last factor is of paramount importance, and retorting is used only for the treatment of specially rich ores. The retorts first employed were made of clay, and cast-iron bottles were later used, and later still retorts made of cast iron were employed shaped much like those used in the preparation of coal gas. The mouth of the retort dipped under water, so that the process is a kind of *distillation per descensum*. At one time, the reduction with iron was used at Horozowitz in Bohemia, and the lime reduction was used in Idria (Carniola), Rhenish Palatinate, Monte Amiata, at Landsberg (Bavarian Palatinate), Pine Flat (California), and is said to be still in use at Lattai (Carniola). The distillation process in Mexico and Chile has been described by B. Neumann, E. de Riviero, V. Perez-Rosales, etc.

The oxidation process includes an air-combustion and a kind of distillation. In an early form of the process employed at Idria,[2] the ore was oxidized on perforated stone arches, and the gaseous products passed from the roasting chamber up and down seven condensing chambers, and finally through a turret-shaped chamber into the air. The inclined floors of the condensing chambers enabled the condensed mercury to be readily collected. This furnace is practically obsolete. At Almaden, the gases from the roasting chambers traversed half a dozen series of tubes made up to small cylinders—called *aludels*—open at both ends, and fitting into one another. These were laid on a surface—called the *aludel-bath*—first descending a little and then ascending, and finally directed into a chimney. This furnace, according to H. Kuss,[3] was designed in 1633 by L. S. Barba in Huancavelica (Peru), and was introduced into Almaden (Spain) by M. Bustamente in 1646, whence it is sometimes called *Bustamente's furnace* or the *aludel furnace*. In spite of many attacks this furnace has maintained itself up to the present. C. de Kalb has described the extraction of mercury at Almaden.

The continuous shaft furnaces are of two types: (i) Those without inclined shelves used for large ore, and exemplified by *V. Spirek's shaft furnace*,[4] and *F. Novak's shaft furnace* without an external fireplace, and A. Exeli's shaft furnace with external heating; (ii) those with inclined shelves used for medium and fine ore, and exemplified by *Scott's shaft furnace*, and *Litchfield's shaft furnaces*. The *Czermak-Spirek Schüttröstöfen* is a kind of *four à cascade* or tile furnace with ridges so arranged as to make it behave like a group of low shaft furnaces or a multiple-hearth reverberatory furnace. The modification without ridges is a reverberatory furnace proper, and is used for dust, ores which decrepitate, and for the treatment of stupp.

V. Spirek's shaft furnace, illustrated by Fig. 1, is a square shaft of ordinary firebrick braced with angle iron and tie-rods, and supported on columns. The bottom of the furnace is about 5 ft. above the floor-line so that a truck can be run underneath to receive the spent ore when the sloping iron firebars are moved. The charge is a mixture of coarse ore with about 2 per cent. of charcoal, and it is fed into the furnace through the hopper. The outlet pipes lead the mercurial vapour, etc., to the condensers. These consist of six or more series of pairs of vertical pipes of cast iron, or glazed stoneware of elliptical cross-section and supported on a wooden framework. Each pair of pipes is about 8 ft. in length, and 20–24 ins. diameter, and is cemented at the bottom into a V-shaped receiver with the lower end open, and dipping into about 2 ins. of water in an iron tank in which mercury and stupp collect. Each pair of pipes is connected with the next by a cap-piece provided with a manhole. The pipes are cooled with water. The gases which leave the condensers pass into a large wooden condensing or dust chamber which is divided by baffle walls so that the gases follow a zig-zag course. This chamber has a sloping floor and gutter to allow any free mercury deposited from the gases to run on to a collecting pan. The exit gases pass from the condensing chamber to the fan and chimney-stack. Every five or ten days there is a clean-up of the tubes with scrapers, brushes, and a jet of water, in order to collect the accumulated stupp.

Mercury is obtained from gold and silver amalgams by distillation. G. H. Mann [5] also describes the recovery of mercury from amalgamation residues. The recovery of mercury from stupp follows on the lines employed for finely-divided ores, and is discussed by C. Schnabel, F. Pilz, G. Goldschmidt and M. von Schmidt, F. Janda, A. Harpf, A. Weiskopf, E. Teuber, etc. The extraction of mercury from fahl-ores has been discussed by C. Schnabel, H. Wedding, J. Schabus, etc. All the commercially successful methods for the extraction of mercury are dry processes; **wet processes** have been proposed, but have met with no economic success. For example, G. Kroupa,[6] C. A. Winkler, and R. von Wagner have proposed to extract mercuric sulphide from its ores by a soln. of an alkali sulphide containing caustic alkalies; R. von Wagner recommended a soln. of barium sulphide, or an aq. or hydrochloric acid soln. of bromine; and T. P. Sieveking proposed a soln. of cuprous chloride in sodium chloride in the presence of a granulated alloy of zinc and copper. The cinnabar is decomposed, $2CuCl+HgS=CuCl_2+CuS+Hg$, and the mercury amalgamates with the zinc-copper alloy, from which it is recovered by distillation.

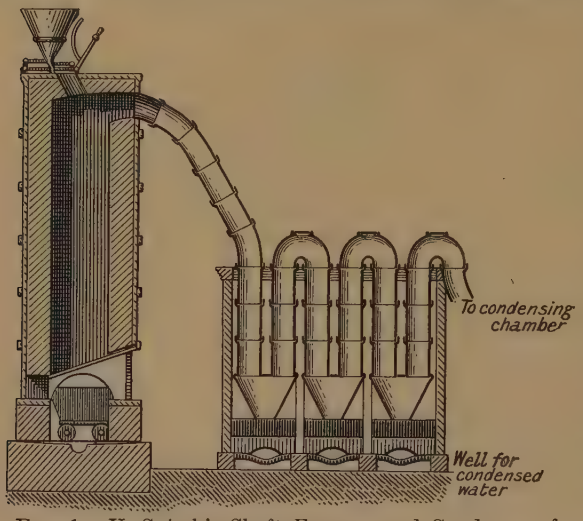

FIG. 1.—V. Spirek's Shaft Furnace and Condensers for Mercury.

The **electrolytic methods** have not been economically successful. A. von Siemens,[7] and B. Szilard electrolyzed a soln. of mercuric sulphide in a soln. of hydrosulphide of calcium, barium, strontium, or magnesium; O. Dammer also suggested electrolyzing a soln. of mercuric sulphide in dil. hydrochloric acid (1 : 10) or in an aq. soln. of sodium chloride.

The reduction of mercury from mercury compounds.—E. Reichardt [8] noticed that precipitated mercurous and mercuric arsenates gradually decompose into mercurous oxide and mercury. M. C. Lea found that by pressing with a pestle in a mortar mercuric and mercurous chlorides, mercuric iodide, and mercuric oxysulphate and oxychloride are decomposed. Several mercury compounds decompose when heated—*e.g.* the oxide, sulphide, chloride, etc. H. Rose found that many mercury salts—*e.g.* mercurous succinate—are gradually decomposed by boiling with water. M. Guerbet found that a soln. of mercuric gluconate is likewise decomposed. P. and M. M. Richter showed that mercurous cyanide decomposes when allowed to stand for some time, or when boiled with water: $2HgCy=Hg+HgCy_2$. L. O. Helmers found aq. soln. of mercurous ichthyolsulphonate behaved similarly. According to J. Riban, a soln. of mercuric acetate in a tube at 175° forms mercury, carbon dioxide, and acetic acid.

Mercuric oxide was found by W. Müller to be reduced to the metal by **hydrogen** at 220°–230°; and O. Schumann found mercuric sulphate to be similarly reduced. N. N. Beketoff, and E. Cohen found that hydrogen precipitates mercury from an aq. soln. of its salts—the press., said C. Brunner, must be over 100 atm. S. Cooke precipitated mercury from soln. of mercuric nitrate by treatment with hydrogenized platinum; and B. Neumann likewise obtained mercury and mercurous chloride from an aq. soln. of mercuric chloride. A. C. Chapman found hydrogenized palladium

reduces soln. of mercuric salts partly to mercurous salts, and partly to metal. F. Utz, and M. Kohn reduced mercuric compounds by the action of **hydrogen peroxide** in alkaline soln., and W. Kwasnik used **barium dioxide.** According to A. Vogel, soln. of mercurous and mercuric salts are reduced to the metal by **sulphur dioxide;** and, according to O. Brunck, **sodium hyposulphite,** $Na_2S_2O_4$, reduces mercury salts to the metal, which is converted into sulphide by an excess of the reducing agent. J. Myers converted mercuric chloride and mercurous nitrate soln. to the metal by means of **potassium hydrosulphide,** KSH. J. Keir found **ferrous sulphate** and **stannous chloride** can reduce mercury salts to the metal. K. Voit reduced mercury compounds by fusion with **alkali carbonates** or **alkali hydroxides ;** and F. Janda by heating them with **iron oxide.**

W. R. Hodgkinson and C. C. Trench passed **ammonia** over heated mercuric sulphate and obtained mercury. A. Thum, and W. Lossen found **hydroxylamine** rapidly reduced mercuric oxide to the metal. E. Knövenagel and E. Ebler found hydroxylamine salts and **hydrazine salts** reduced alkaline soln. of mercuric salts and also soln. feebly acidified with acetic acid. T. Curtius and F. Schrader, A. Purgotti, E. Rimini, and P. Jannasch and W. Bettges also studied the reduction with hydrazine salts. An alcoholic soln. of mercuric cyanide is reduced by **stibine.** B. E. Howard reduced mercury compounds to the metal with **hypophosphorous acid.** A. Gutmann reduced mercury fulminate with an alkaline soln. of **arsenious acid ;** I. Pouget with **potassium thioantimonite ;** and P. Pascal, with **sodium ferric pyrophosphate.**

A. C. Becquerel reduced mercuric oxide by heating it with **carbon**—*vide infra.* N. Tarugi reduced mercuric compounds by heating them with **calcium carbide.** Many organic compounds reduce mercury salts to the metal, and the reaction is often accelerated by heat or by exposure to light. Thus, A. Vogel found **cane sugar** reduced soln. of mercurous nitrate to mercury and a little mercuric oxide ; F. Soxhlet reduced alkaline soln. of mercury salts to the metal. J. Stern and S. Fränkel used an alkaline soln. of **invert sugar ;** and J. von Liebig, and C. Knapp reduced an alkaline soln. of mercuric cyanide completely to the metal, by means of **grape sugar.** F. Göbel and P. A. von Bonsdorff found **formic acid** and alkali formates reduce mercury compounds to the metal. O. Loew, and E. Feder have studied the reduction of mercury compounds with **aldehyde,** J. M. Eder investigated the reducing action of **potassium ferrous oxalate** on mercuric salts. C. K. von Reichenbach, of **creosote ;** M. J. B. Orfila, **turpentine ;** M. T. Lecco, and W. Brunetti, vegetable and animal substances ; G. Bizio, **gelatine ;** etc. H. Moissan reduced mercurous chloride by heating it to 700° with **boron.**

The metallic precipitation of mercury.—According to N. W. Fischer,[9] copper, zinc, cadmium, arsenic, antimony, bismuth, tin, lead, and iron precipitate mercury from soln. of mercurous nitrate ; with copper, zinc, cadmium, lead, and bismuth, the precipitation is complete in 24 hrs., but with the other elements, some mercury remains in soln. In some cases a white or yellow precipitate—*e.g.* bismuth and lead—is formed at the same time. If a soln. of mercuric nitrate is employed, the action is slower, the salt is first reduced to mercurous nitrate, and basic salts are precipitated with copper, zinc, cadmium, bismuth, antimony, and lead. With soln. of mercuric chloride, zinc, cadmium, and nickel precipitate mercury rapidly and completely, with iron the action is slower, and slower still with copper, bismuth, and lead—in most cases also some mercurous chloride is precipitated at the same time ; with zinc and cadmium, an amalgam is formed. P. Schorigin found that mercury is obtained when mercuric ethyl is treated with **sodium ;** and at 100°, E. Frankland and B. F. Duppa observed that the mercury in this compound is completely displaced by zinc, and more slowly and not completely by cadmium, copper, silver, gold, bismuth, and iron. E. Alexander found that mercury is displaced from a soln. of mercuric chloride in ethyl acetate by **aluminium,** and magnesium, and partially by copper, zinc, tin, lead, antimony, and bismuth.

When **copper** is immersed in a soln. of a salt of mercury, the metal becomes

covered with a grey film which appears silvery white when rubbed between paper. H. Reinsch found that copper is coated by a film of mercury in a soln. of mercuric chloride (1 : 1000) in the presence of hydrochloric acid ; with a dilution of 1 : 50000, no film is produced in the cold if the acid be absent, but when boiled the copper is coloured golden-yellow, and if the acid be present, a grey film of mercury is produced. A. Vogel found the film is lost when the copper stands exposed to the air for 12 hrs. T. W. Richards and S. K. Singer obtained a quantitative precipitation of mercury from a soln. of mercuric nitrate with not too great an excess of acid ; and, according to W. Odling, and H. G. Magnus, the precipitation occurs with soln. of mercuric chloride, but not with soln. of mercuric sulphate or nitrate. M. Caucal, and A. Vogel obtained mercurous chloride as well as mercury from soln. of mercuric chloride. N. W. Fischer also found that mercury is reduced from a soln. of a mercurous salt by brass. According to A. Ogg, dil. soln. of mercurous salts are reduced by **silver,** and, according to J. N. Brönsted, 1·29 to 1·55 Cals. are absorbed per mol of mercurous chloride, and more at a higher temp. C. Zenghelis found that silver foil reduces a cold sat. soln. of mercuric nitrate, and in 2 hrs. at 80°, a soln. of mercuric chloride is reduced to mercurous chloride. G. Campani found that in a few hours finely divided silver completely reduces to mercury an aq. soln. of mercuric chloride, or an aq. soln. of potassium iodide and mercuric iodide. G. McP. Smith also noted the reductions of soln. of mercuric chloride, cyanide or nitrate, mercurous nitrate, or of potassium mercuric cyanide. A. Vogel found that with mercuric chloride soln., some mercurous chloride is precipitated as well, and G. Wetzlar noted the production of silver chloride. E. Cohen, and A. and L. Lumière and A. Seyewitz studied the bleaching of photographic negatives in consequence of the reaction : $Ag+HgCl_2=AgCl+HgCl$. N. W. Fischer found that alloys of silver with tin, lead, zinc, and copper reduce soln. of mercurous salts to mercury. G. Bredig and J. Weinmayr noted that **gold** precipitates mercury from a conc. soln. of potassium mercuric cyanide ; and if an alkaline soln. of mercuric chloride be treated with colloidal gold, mercury is precipitated on the particles of gold.

According to A. Schmidt, and K. Seubert, **magnesium** precipitates from neutral soln. of mercuric chloride, a mixture of mercurous chloride, mercury, and mercuric oxide, and the precipitation is complete, only after a prolonged boiling ; in acid soln., more mercury is mixed with the mercurous chloride. If mercurous chloride suspended in water be boiled for several hours with magnesium filings, mercury mixed with a little mercurous oxide is quantitatively obtained—in the presence of hydrochloric acid, the latter is not formed. S. Kern found that magnesium with a conc. soln. of mercuric chloride furnishes hydrogen and mercuric oxide ; and H. Mouraour noted that the separation of mercury by the magnesium treatment is attended by the evolution of hydrogen. D. Vitali found that with magnesium a conc. soln. of mercuric chloride gives hydrogen, mercuric oxide and oxychloride, mercurous oxide and the metal ; with mercuric cyanide, magnesium cyanide is formed which decomposes at a low temp., forming magnesium oxide, which then forms some mercuric oxide, and a part of the evolved hydrogen reduces the mercuric cyanide, and oxide to mercury. According to H. Rose, **zinc** does not reduce an aq. soln. of mercurous sulphate, or mercurous chloride suspended in water ; zinc precipitates all the mercury from soln. of mercuric sulphate or nitrate acidified with sulphuric or nitric acid, or from neutral soln. of mercuric chloride, without amalgamation, but a soln. of mercuric chloride acidified with hydrochloric acid rapidly amalgamates the zinc. E. Ludwig found zinc precipitates all the mercury from urine. R. Varet found that **aluminium** precipitates mercury from aq. soln. of mercuric cyanide, and A. Cossa, from aq. soln. of mercuric nitrate or chloride—some aluminium hydroxide and hydrocyanic acid are produced in the former case—the mercury unites with the aluminium, forming an amalgam which vigorously decomposes water, and rapidly oxidizes in air. V. Borelli stated that aluminium is better than magnesium or zinc for reducing mercury from cyanides. J. Klaudy found

that with a soln. of mercuric chloride, aluminium amalgam is formed which decomposes water, forming aluminium hydroxide ; F. Regelsberger noted the formation of aluminium hydroxide in this reaction. C. Reichard noted that insoluble or sparingly soluble mercury compounds react with aluminium feebly or not at all.

L. F. Boeck, and M. Lazowsky found that **carbon** immersed for two days in a soln. of mercurous nitrate becomes covered with globules of mercury. N. W. Fischer found that with a soln. of mercurous nitrate, **tin** becomes covered with a brown powder which continually deepens in colour and after a few days is resolved into globules of mercury. According to J. Smithson, if a piece of tin in contact with a gold plate is introduced into a soln. of a mercuric salt acidified with hydrochloric acid, the tin forms an amalgam with the precipitated mercury. J. H. van den Broek obtained a similar result with a tin-platinum couple. E. Rupp reported that **iron** quantitatively precipitates mercury from mercuric salts, and M. J. B. Orfila, that iron decomposes mercurous salts at ordinary temp. ; but N. W. Fischer said that iron has no action on a soln. of mercurous nitrate because the metal becomes passive, and L. Gmelin added that this applies to a conc. soln. of mercurous nitrate, but from a dil. soln. of the nitrate or acetate, mercury is readily precipitated. R. Varet found that iron is a stronger reducing agent than **nickel,** and that the latter metal reduces an aq. soln. of mercuric chloride to mercurous chloride, and partially to mercury—if air is present some nickel sesquioxide is formed. E. F. Smith observed that **molybdenum** reduces soln. of mercuric chloride, potassium mercuric iodide, and mercurous sulphate to the metal. E. F. Smith found that **tungsten** slowly reduces aq. soln. of mercuric chloride to the mercurous chloride, but soln. of mercurous sulphate and potassium mercuric iodide are only partially reduced. C. Zimmermann found that **uranium** precipitates mercury from a soln. of mercuric nitrate, and a mixture of the metal and mercurous oxide from a soln. of mercuric chloride.

According to H. Davy, when **phosphorus** vapour is passed over heated mercuric chloride, it forms phosphorus trichloride and the metal. L. F. Boeck, and N. W. Fischer observed that phosphorus precipitates mercury from a soln. of a mercurous salt. M. J. B. Orfila found that **arsenic** precipitates mercury from mercurous nitrate or sulphate at ordinary temp., and N. W. Fischer, that **antimony** does not precipitate mercury from a soln. of mercuric chloride. The action of **bismuth** is indicated above.

The electro-deposition of mercury.—The quantitative precipitation of mercury by the electrolysis of soln. of its salts is discussed in several text-books—*e.g.* those of A. Fischer,[10] A. Classen, and E. F. Smith—and the subject has been discussed by F. Rüdorff, H. J. S. Sand, J. B. Hannay, C. H. Wolff, A. Fischer, C. Luckow, Z. Karaoglanoff, etc. In the electrolysis of mercurous nitrate soln., N. W. Fischer obtained some peroxide, and basic nitrate. A. Classen, and L. de la Escosura showed that the electrolysis of aq. soln. of sodium chloride or hydrochloric acid in which insoluble mercury compounds—mercuric sulphide, mercurous chloride, etc.—are suspended yield mercury ; F. W. Clarke also found that mercury is precipitated from a soln. in which the basic sulphate is suspended. Electrodes for the electrolysis of mercury salt soln. have been investigated by A. Classen, S. K. Singer,[11] and many others.

An electrolyte acidified with *nitric acid* was employed by A. Classen, H. Freudenberg,[12] E. F. Smith and co-workers, R. O. Smith, H. J. S. Sand, etc. ; an electrolyte acidified with *sulphuric acid*, by F. W. Clarke,[13] L. G. Kollock, A. Fischer, E. Bindschedler, and B. Neumann ; *ammoniacal* electrolytes, by H. J. S. Sand,[14] and M. François ; an electrolyte containing *cyanides* by E. F. Smith [15] and co-workers, F. Glaser, E. Bindschedler, A. Classen, etc. ; a soln. of *ammonium or potassium thiocyanate* by L. K. Frankel ; [16] a soln. of mercuric sulphide in *sodium sulphide* by E. F. Smith and co-workers, L. G. Kollock, A. Fischer, R. O. Smith, G. Vortmann, etc. ; [17] a soln. of mercuric chloride in one of *potassium iodide*, by G. Vortmann ; [18] a soln. of *sodium or ammonium phosphate* in one of ammonia or

ammonium carbonate, by F. Rüdorff, A. Brand, H. M. Fernberger and E. F. Smith, etc.; [19] a soln. of a mercury salt in an excess of a soln. of *ammonium oxalate*, by A. Classen, G. Vortmann, and A. Fischer; [20] a soln. of a mercury salt in an excess of ammonia and *ammonium tartrate*, by G. Vortmann, S. C. Schmucker, and F. Rüdorff; [21] and a soln. of *mercuric chlorate*, by F. G. Mathers and A. F. O. Germann.[22]

The purification of mercury.—Mercury should leave no residue when dissolved in nitric acid, or when fused with sulphur and sublimed in a glass flask; and when agitated with dry air, it should not yield any black powder. When contaminated with foreign metals, etc., mercury becomes *extinguished*, *sickened*, or *deadened*. Consequently, when a globule of mercury is made to run down a gently inclined surface, it should retain its spheroidal form, and not "leave a tail." According to M. Meier,[23] the "tail" consists largely of an amalgam of foreign metals with much adherent mercury. According to C. Michaelis, the electrical conductivity is a very sensitive test for the purity of mercury, and G. A. Hulett and H. D. Minchin state that this method will detect the presence of one part of zinc in 10 billion parts of mercury. Impurities mechanically mixed with the mercury can be removed by filtration by press. or suction through leather, or through perforated paper as recommended by L. Pfaundler, G. F. Hildebrandt, G. Vulpius, etc. Several methods have been proposed for the more or less incomplete purification of mercury, and some of these rapid processes are useful in a laboratory where a freely flowing liquid for confining gases, etc., is required, and not necessarily a highly purified metal for chemical operations. W. C. Röntgen has discussed the preparation of mercury presenting a clean surface.

In the method of oxidation a stream of air is drawn through the liquid, and many foreign metals associated with the mercury are oxidized and the grey pulverulent mixture of oxides can be removed by filtration through leather as recommended by J. M. Crafts, L. C. Barreswil, J. J. Berzelius, P. Baumann, E. Maumené, etc. The mercury can also be shaken with certain liquids which oxidize and in some cases dissolve the impurity—thus, G. Branchi recommended agitating the impure mercury for some days with sulphuric acid, or boiling the impure mercury with $\frac{1}{87}$th of its weight of mercurous nitrate dissolved in a small quantity of very dil. nitric acid; W. Ostwald and R. Luther, and T. W. Richards and G. S. Forbes, a 5 per cent. soln. of mercurous nitrate mixed with some nitric acid; C. Michaelis, shaking with sulphuric acid mixed with a little nitric acid until the mercury was broken up into small globules; G. L. Ulex and H. Wild, a soln. of ferric chloride of sp. gr. 1·48; L. J. Desha, one per cent. nitric acid; G. A. Hulett and H. D. Minchin, an excess of mercurous sulphate in dil. sulphuric acid (1 : 10); J. W. Brühl, W. Kerp, G. McP. Smith, and W. Bolton, a soln. of 5 grms. of potassium dichromate in a litre of water acidified with a few c.c. of sulphuric acid; F. G. Voigtel, a boiling soln. of mercuric chloride in a clean iron vessel—but G. C. Wittstein said this process is not good because mercurous chloride is formed; W. R. Forbes, charcoal sat. with oxygen gas; H. W. F. Wackenroder, a soln. of hydrochloric acid mixed with one-eighth vol. of sulphurous acid; and W. Bettel, a dil. soln. of potassium cyanide in the presence of sodium peroxide—it is claimed that this treatment removes gold, zinc, tin, lead, copper, and iron, and leaves the mercury of a higher degree of purity than fractional distillation. In the shaking process, the surface of contact between the metal and the soln. is relatively small, and a long shaking is required to dissolve the impurities present in the mercury; L. Meyer, and A. Weinhold therefore proposed allowing the mercury to fall in a fine stream one or more times through a long column of mercurous nitrate. Several forms of apparatus have been proposed—*e.g.* by B. Karsten, C. Harries and F. Evers, K. Kaehler and M. Martini, C. J. Moore, G. A. Hulett and H. D. Minchin, J. H. Hildebrand, L. J. Desha, etc. In some of these forms, the mercury is raised by suction to the upper part of the apparatus so that the process is continuous, and the mercury descends through the column of liquid a number of times.

W. Jäger, and F. A. Wolff and C. E. Waters purified mercury electrolytically

by making the impure mercury the anode in a soln. of nitric acid ; J. H. Hildebrand added that the process occupies much time, requires efficient stirring, and is not particularly efficacious. According to C. Michaelis, the separation of mercury from admixed impurities is complete if the impure mercury be distilled in vacuo, with the surface of the metal at rest ; if the press. be insufficiently low, and the surface of the mercury turbulent, some spray of impure metal is carried along with the vapour to the receiver. Boiling mercury is liable to spirting—covering the impure mercury in the retort with a thick layer of iron filings in order to arrest the spray has been recommended ; and A. F. L. Dörffurt recommended distilling the mercury with one-tenth its weight of cinnabar ; he believes that the sulphur retains the foreign metals in the retort. H. Violette recommended distilling silver-amalgams in a current of superheated steam. Even if bumping be prevented it is probable that some zinc, cadmium, lead, tin, bismuth, and copper can vaporize with the mercury. V. Meyer has said :

> It is commonly assumed that mercury can be purified by distillation, but, even after three distillations, much impurity remains. It is therefore possible that the mercury vapour carries with it the vapours of other metals as when substances are distilled in a current of steam, or that the impure mercury is mechanically carried forward as spray. In order to determine which of these possibilities is correct, mercury was mixed with a number of metals—lead, bismuth, tin, sodium, and copper—and the mixture distilled first from a porcelain retort and then repeatedly distilled from a glass retort. After twelve distillations, no trace of residue remained in the glass retort, and the distillate gave no residue when two grams of the metal were dissolved in nitric acid, the soln. evaporated, and the residue calcined in a weighed platinum dish.

G. A. Hulett and H. D. Minchin have shown that unless mercury is distilled in a current of air and with no bumping, the more volatile metals like zinc and cadmium are not removed. The distillation process, and various forms of mercury still have been recommended by L. C. Barreswil, W. D. Bohm, H. M. Chance, J. W. Clark, L. Dunoyer, W. R. Dunstan and T. S. Dymond, F. Friedrichs, F. A. Gooch, G. F. Hildebrandt, B. Karsten, B. Lambert, R. Leeds, L. Meyer, N. A. E. Millon, H. N. Morse, B. Nebel, J. Pollak, F. J. Smith, A. Weinhold, J. Wetzel, A. W. Wright, etc. C. T. Knipp heated the mercury to be distilled by striking an arc between the surface of the mercury and each of two electrodes. The mercury was kept in vacuo, and the mercury in the interior of the glass vessel was in communication with that outside. G. A. Hulett recommended distilling the mercury at about 200° in a distillation flask so arranged that a stream of nitrogen or carbon dioxide was drawn through a fine capillary tube below the surface of the mercury, while the interior was under a press. of 25 mm. An amalgam sat. with silver gave a distillate with one of silver in 1,000,000 parts of mercury, and no silver could be detected in the second distillate ; a gold amalgam likewise gave a first distillate with 27 parts of gold in 1,000,000,000 parts of mercury, and no detectable amount of gold in the second distillate ; similarly, the first distillate of a platinum amalgam contained one of platinum in 100,000,000 parts of mercury.

In the more strictly chemical methods of purification, the mercury is converted into some salt and the purified product is reduced. Thus, C. F. Mohr heated purified mercuric oxide, and obtained a product covered with a film of reproduced oxide. This was purified by shaking with dil. sulphuric acid. G. N. Lewis and R. F. Jackson, and V. Meyer also obtained mercury from the purified oxide. G. F. Hildebrandt heated the purified sulphide or chloride with one part of lime or iron filings—preferably the former.

Colloidal mercury.—If mercury be agitated with water, ether, turpentine, acetic acid (R. Böttger),[24] or various salt soln.—calcium or ammonium chloride, sodium nitrate, etc. (N. A. E. Millon)—aq. mercuric chloride or dil. nitric acid (F. B. Hofmann), garlic juice (M. N. Banerjee), or if it be triturated with sulphur, antimony sulphide, sugar, grease, etc., even in vacuo, the mercury is converted into a grey emulsion—*æthiops per se*—which consists of minute globules of mercury separated by another medium. The particles coalesce by running together when the

medium is withdrawn, so that the mercury in the emulsion is not sickened mercury—a subject discussed by L. V. Brugnatelli, L. J. Proust, J. Roux, I. Walz, etc. F. V. Bärensprung stated that some of the mercury in grey mercurial ointment is in the state of mercurous oxide—the older the ointment the greater the proportion of black oxide. By first extracting the fat with ether, the oxide can be washed from the residue by water acidulated with sulphuric acid. M. Donovan and K. Voit assumed that mercurous salts of the fatty acids were formed, but A. J. von Oettingen showed that neither mercurous oxide nor the fatty acid salt is present; and C. Barfoed showed that the finely divided mercury does not oxidize in air at ordinary temp. The grey powder is an emulsion consisting of finely divided mercury suspended in the medium. J. Sen stated that finely divided mercury is grey not black. The particles of mercury in grey mercurial ointment cannot be distinguished by the eye alone, and, according to C. G. Ehrenberg, they are nearly uniform in size and range between 0·001 and 0·002 mm. in diam.

Colloidal mercury has been obtained by A. Westgren,[25] A. Schereschewsky, A. Gutbier and G. L. Weise, I. Nordlund, J. Billitzer, H. Finger, L. Egger, and F. Haber, by electrolysis, or by cathodic disintegration. The preparation of the colloid by the action of liquid ammonia on mercuric chloride was described by W. Weyl,[26] and J. Bronn; by the action of aq. ammonia on a dil. soln. of mercurous nitrate or mercuric chloride in 5 per cent. gelatine, by C. A. L. de Bruyn; by the reducing action of hydrazine salts by A. Gutbier and G. Hofmeier,[27] R. May, and A. Lottermoser; by hydroxylamine in the presence of sodium resinate, by A. Westgren; by the action of stannous salts by A. Lottermoser,[28] M. Höhnel, J. L. Mewburn, J. Billitzer, and C. A. L. de Bruyn; by the action of colloidal gold, by J. Weinmayr,[29] and G. Bredig and W. Reinders; and by the action of salts of protalbinic or lysalbinic acid, by G. Amberger,[30] and M. K. Hoffmann. The latter reduced the soln. of a mercury salt by the action of dil. soln. of alkali hydroxide or carbonates followed by dialysis; A. Lottermoser, with ammonium citrate; J. Meyer, with sodium hyposulphite, $Na_2S_2O_4$; A. Gutbier, with hypophosphorous acid; P. Pascal, with ferrous pyrophosphate; F. Küspert, with water-glass and formaldehyde; F. Henrich, with pyrogallol; and A. Dering, with triglycerides; and H. N. McCoy and co-workers, by the electrolysis of cold soln. of tetramethylammonium chloride in absolute alcohol, and a mercury cathode—the tetramethylammonium amalgam decomposes when treated with water, forming colloidal mercury. The *hyrgol* of commerce is colloidal mercury containing 73–80 per cent. of the metal. C. Foa and A. Aggazzotti studied the oxidizing action of colloidal mercury in the presence of hydrogen peroxide. I. Nordlund examined the properties of mercury hydrosols prepared by different processes.

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§ 3. The Physical Properties of Mercury

At ordinary temp. mercury is a coherent, mobile, silvery-white liquid, which has very little tendency to adhere to glass. According to L. H. F. Melsens,[1] the **colour** of very thin layers of mercury in transmitted light is blue with a violet tinge ; and, according to F. P. le Roux, the vapour of mercury is blue. G. F. Hildebrandt said that mercury has no odour, and that it *schmerkt metallisch*. H. B. Dixon found that chemically inert gases may be confined over mercury without any appreciable change in volume, showing that the metal is not permeable to these gases. M. Faraday's observation that gases could escape when confined in glass jars in a pneumatic trough over mercury has not been confirmed. Mercury

freezes to a crystalline mass which, according to T. des Coudres, is anisotropic. L. Bleekrode described the freezing of mercury by the aid of solid carbon dioxide; B. Schwalbe used a mixture of solid carbon dioxide and ether. R. Walker stated that the frozen solid consists of octahedral and acicular **crystals**; and that the crystalline mass is a ductile metal with a granular fracture. The crystals have not been so closely investigated as those of the other members of the zinc family of elements; C. F. Rammelsberg stated that the solid metal has a cubical cleavage. According to N. A. Puschin, tin and cadmium amalgams crystallize in the hexagonal system, and the position of mercury in the periodic system with beryllium, magnesium, zinc, and cadmium, all of which form hexagonal crystals, makes it probable that mercury crystals will prove to be hexagonal. M. Volmer studied the growth of the crystals. N. Alsen and G. Aminoff found that the **X-radiogram** of mercury at the temp. of solid carbon dioxide, corresponded with a hexagonal cell containing four atoms and having $a=3{\cdot}84$ A., and $c=7{\cdot}24$ A. The X-radiogram of mercury, taken by L. W. McKeehan and P. P. Cioffi, agrees with a rhombohedral space lattice with an axial ratio $a:c=1:1{\cdot}94$.

The physical properties of mercury have been the subject of numerous investigations. H. Fritz,[2] and A. Schulze have made collections of the physical constants of this element. The Arabic manuscript of Abu-r-Raihan, *The Book of the Best Things*, written about the tenth century, and described by H. C. Bolton, and J. J. Clément-Mullet, has a table of **specific gravity** of 19 substances, and it includes liquid mercury, with a sp. gr. 13·58, which is very near the value accepted to-day. In the Arabian manuscript *Book of the Balance of Wisdom*, written by Al-Khazini in the years 1121–1122 A.D., and described by H. C. Bolton, and N. Khanikoff, 13·56 is given for the sp. gr. of mercury.

G. D. Fahrenheit gave 13·575; P. van Muschenbroek, 13·550; R. Boyle, 14·000; H. Cavendish and M. J. Brisson, 13·5681; J. B. Biot and D. L. J. Arago, 13·588597; C. J. B. Karsten, 13·5592; J. Crichton, 13·568 (15·5°); R. Scholz, 13·586; H. Schiff, 13·603 (12°); P. Volkmann, 13·5953 (0°); H. Kopp, 13·595 (0°); B. Stewart, 13·594 (13·6°) in vacuo; A. F. Kupffer, 13·5886 (4°/4°), and 13·535 (26°/4°); A. W. Warrington, 13·59563 at 0°; J. Biddle, 13·613 (10°); A. Matthiessen, 13·573 (14·5°); and H. Wild, and W. Marek, 13·5956 (0°/4°).

G. Vicentini and D. Omodei found 13·6902 at −38·85°—*i.e.* for the liquid at the f.p. G. G. Hällström obtained 13·6078 (0°), and 12·810 at the b.p.; and H. V. Regnault, 13·582 (5°–10°), 13·570 (10°–15°), 13·558 (15°–20°), and 13·59593 at 0°. R. Lenz and N. Restzoff obtained the extremes 13·59869 and 13·59810 for determinations with thirteen different samples of mercury. M. Thiesen and K. Scheel gave 13·59545 at 0°. The best representative value of this mass of discrepant data may be taken as 13·596 at 0°. R. Walker found that the solid metal is specifically heavier than the liquid because it sinks therein. J. A. Schultze gave 14·391 for the sp. gr. of solid mercury; G. G. Hällström, 14·333 at −40°; J. Biddle, 14·485 at −60°; J. W. Mallet gave 14·1932 for the sp. gr. of the solid at −38·85°, water at 4° unity; J. Dewar gave 14·382 for the sp. gr. at the temp. of liquid air, say −188°. By extrapolation from the average of 36 determinations of the sp. gr. of solid amalgams, J. P. Joule estimated the sp. gr. of solid mercury to be 15·19. A. W. Warrington gave for the vol., v, at a temp. $\theta°$, not exceeding 40°, $v=v_0(1+0{\cdot}0001819\theta)$. P. Chappius represented his measurements of the vol. v at $\theta°$ for temp. below 0°, by $v=v_0(1+1{\cdot}815405\times10^{-4}\theta+1{\cdot}195130\times10^{-8}\theta^2+1{\cdot}00917\times10^{-10}\theta^3-2{\cdot}03862\times10^{-8}\theta^4)$; and for temp. above 0°, $v=v_0(1+1{\cdot}816904\times10^{-4}\theta-2{\cdot}951266\times10^{-9}\theta^2+1{\cdot}14562\times10^{-10}\theta^3)$, where v_0 represents the vol. at 0°. J. Bosscha gave $v=2^{0{\cdot}000180776\theta}$. J. W. Mallet gave 14·193 at its m.p.; and J. Dewar, 14·382 at the temp. of liquid air. M. Thiessen, K. Scheel, and L. Sell represent their results by

$$v=v_0\left\{1+0{\cdot}018161\frac{\theta}{100}+0{\cdot}000078\left(\frac{\theta}{100}\right)^2\right\}$$

Tables I and II, respectively denoting the sp. gr. and sp. vol. of mercury between −20° and 360°, are compiled from the results of M. Thiessen, K. Scheel, and L. Sell

TABLE I.—THE SPECIFIC GRAVITY OF LIQUID MERCURY BETWEEN −20° AND 360° (SPECIFIC GRAVITY OF WATER AT 4° UNITY).

°C	0	1	2	3	4	5	6	7	8	9
−2	13·64499									
−1	2017	2265	2513	2761	3009	3257	3505	3754	4002	4251
−0	13·59545	9792	*0039	*0286	*0533	*0780	*1027	*1275	*1522	*1770
+0	9545	9298	9051	8804	8558	8311	8065	7818	7572	7326
1	7079	6833	6587	6341	6095	5849	5604	5358	5113	4867
2	4622	4376	4131	3886	3641	3396	3151	2906	2661	2416
3	2171	1927	1682	1437	1193	0949	0704	0460	0216	*9972
4	13·49728	9484	9240	8996	8752	8508	8265	8021	7778	7534
5	7290	7047	6804	6561	6317	6074	5831	5588	5345	5102
6	4859	4616	4373	4131	3888	3646	3403	3160	2918	2675
7	2433	2191	1949	1706	1464	1222	0980	0738	0496	0254
8	0012	*9770	*9528	*9287	*9045	*8803	*8562	*8320	*8078	*7837
9	13·37595	7354	7113	6871	6630	6389	6148	5906	5665	5424
10×1	13·3518	3283	3044	2805	2567	2330	2093	1856	1624	1384
10×2	1148	0913	0678	0443	0209	*9975	*9741	*9507	*9273	*9039
10×3	12·8806	8572	8339	8105	7872	7638	7405			

TABLE II.—THE VOLUME OF LIQUID MERCURY BETWEEN −20° AND 360° (VOLUME OF WATER AT 4° UNITY).

°C	0	1	2	3	4	5	6	7	8	9
−2	0·0732870									
−1	4205	4071	3938	3804	3671	3537	3404	3270	3137	3003
−0	5540	5407	5273	5140	5006	4873	4739	4606	4472	4338
+0	5540	5674	5807	5941	6075	6208	6342	6476	6609	6743
1	6877	7010	7144	7278	7411	7545	7679	7812	7946	8080
2	8213	8347	8481	8615	8748	8882	9016	9150	9284	9417
3	9551	9685	9819	9953	*0087	*0221	*0354	*0488	*0622	*0756
4	0·0740890	1024	1158	1292	1426	1560	1694	1828	1962	2096
5	2230	2364	2499	2633	2767	2901	3035	3170	3304	3438
6	3572	3707	3841	3975	4110	4244	4378	4531	4647	4782
7	4916	5051	5185	5320	5454	5589	5723	5858	5993	6127
8	6262	6397	6531	6666	6801	6936	7071	7205	7340	7475
9	7611	7745	7880	8015	8150	8285	8420	8556	8691	8826
10×1	8939	*0285	*1633	*2982	*4334	*5688	*7044	*8402	*9764	**61128
10×2	0·0762495	3865	5239	6616	7996	9381	*0769	*2161	*3558	*4958
10×3	0·0776364	7774	9189	*0609	*2033	*3464	*4900			

—*e.g.* the sp. gr. of mercury at 250° is 12·9975. L. P. Cailletet, E. Colardeau, and A. Rivière gave for the sp. gr. of liquid mercury at high temp. (Fig. 4):

	500°	600°	800°	900°	1000°	1100°	1200°	1270°	1320°
Sp. gr. . .	12·5	12·15	11·6	11·15	10·55	10·0	8·85	8·25	7·8

A. C. Cousins, A. J. Hopkins, R. Lorenz, and E. Donath and J. Mayrhofer have discussed the relations between the sp. gr. and at. vol. of mercury with those of the other elements. J. N. Brönsted and G. von Hevesy observed no measurable difference in the sp. gr. of mercury of different geological and geographical origin.

The **vapour density** of mercury, air unity, has been measured by A. Bineau,[3] who gave 6·7 (882°); J. B. A. Dumas, 6·976; E. Mitscherlich, 7·03; when the

theoretical value for the mol. wt. 200 is 6·93, and L. Troost obtained this value at 18·5°. V. Meyer obtained 1·97(H_2=2) at 1500°; and 2·02 at 1731°. Concordant results were obtained by A. Scott, H. von Wartenberg, H. B. Baker, W. J. Kurbatoff, and F. B. Jewett. J. Bender gave for the vap. density, water unity (Fig. 4):

	1050°	1210°	1230°	1295°	1330°	1380°
Vapour density . .	0·70	1·15	1·35	1·65	1·90	2·50

C. T. Heycock and F. H. Neville estimated the **molecular weight** of mercury from the f.p. of soln. in sodium, cadmium, tin, lead, and bismuth. M. N. Saha gave 0·69 Å. for the at. radius of mercury.

J. R. Rydberg[4] gave 1·5 for the **hardness** of mercury, and J. C. Bull and E. M. Lagerwall found that a little mercury introduced as lead- or tin-amalgam can be used to modify the hardness of some alloys. The **surface tension** of mercury has been the subject of many investigations. For mercury in air, P. S. de Laplace[5] found 44·05 mgrms. per mm.; S. D. Poisson, 44·21; F. Basforth and J. C. Adams, 34·00; P. Desains, 45·97 (20°); J. Magie, 45·82 (20°); E. Sieg, 46·44 (20°); M. Cantor, 45·89 (20°); L. Grunmach, 50 falling to 40 (18°); G. Quincke, 45·78 (20°); H. Siedentopf, 45·40 (20°); and G. Meyer obtained the extremes 43·68 and 51·5 (18°); H. Sentis, 39·23 (20°); J. Stöckle, 44·40 (17°); P. Lenard, 47·10 (20°); J. Piccard, 50·00; L. Matthiessen, 48·3 (20°); M. Smith, 53·9 (20°); and A. Kalähne, 44 (18°). R. Cenac, J. L. R. Morgan, E. Rothé, and C. T. R. Wilson have also discussed the measurement of this constant. The results are not very concordant, the observations are very sensitive to impurities on the surface of the mercury. W. D. Harkins and E. H. Grafton obtained 464 dynes in air, and 374·8 dynes in water; and S. W. J. Smith gave 447·5 dynes per cm. at 15°–17°. J. Palacios found 402 dynes per cm. for specially purified mercury in vacuo. The value for this constant with fresh surfaces of mercury is greater in some gases than in air. J. Stöckle, and G. Meyer found at 15°, 44·4 mgrms. per mm. in vacuo; 48·8 to 51·5 in air; 48·7 to 51·4 in oxygen; 49·8 to 50·5 in nitrogen; 47·9 to 56·5 in hydrogen; and 49·0 to 49·6 in carbon dioxide. J. G. Popesco examined the effect of ammonia, and of sulphur dioxide on the surface tension of mercury, and concluded that the effects are due to the adsorption of the gas by the mercury; J. Palacios and E. Lasala found no difference between the effect in oxygen and in vacuo. The surface tension of mercury in gases decreases with time until it approximates to the value it has in vacuo. This change is not due to the formation of a film derived from the vapour of a fat, but rather to the condensation of gas on the surface of the metal. The best representative value for mercury sat. with air lies between 44 and 46 mgrms. per mm. A. M. Worthington found the surface tension between mercury and water to be 377 dynes per cm.; G. Quincke and M. Lenkewitz gave 370. A. H. Bucherer found the surface tension of mercury is decreased in a soln. of a mercuric salt. G. Quincke, F. R. Watson, M. Lenkewitz, G. Meyer, L. Grunmach, F. Paschen, A. Gouy, H. Pellat, A. Berget, O. Wiedeburg, A. König, S. W. J. Smith and H. Moss, F. Krüger, H. Luggin, G. Lippmann, J. J. van Laar, G. Kucera, G. von Hevesy and R. Lorenz, W. Nernst, etc., measured the effect with a number of soln. of acids, alkalies, and salts; and also with a number of liquids. Thus, in mgrms. per mm. at 20°

Water.	Alcohol.	Benzene.	Olive oil.	Petroleum.	Amyl alcohol.	Turpentine.
37·47	37·33	33·5	31·0	26·0	25·5	23·4

The lowering of the surface tension follows the order: sulphuric acid, salicylic acid, picric acid, and neo-fuchsine, and the adsorption from the soln. increases in the same order. W. C. McC. Lewis investigated Gibb's equation for adsorption by mercury; R. W. Wood studied the damping effect of castor oil and glycerol on the surface waves of mercury. G. Jäger represented the effect of temp. on the surface tension, σ, of mercury in air by $\sigma=\sigma_0(1-0{\cdot}00013\theta)$, where σ_0 is the value at 0°; and H. Siedentopf gave 0·000351 for the temp. coeff. M. Petrowa found no measurable difference in the curvature of a globule of liquid and of solid

mercury. T. R. Hogness gave $\sigma=467-0{\cdot}043(\theta+39)-0{\cdot}000386(\theta+39)^2$ for the surface tension of mercury at $\theta°$. W. Hagemann gave $\sigma=472{\cdot}1-0{\cdot}148\theta-0{\cdot}000344\theta^2$ dynes per cm.; and for the mol. surface energy $k=d\{T(M/D)^{\frac{2}{3}}\}/d\theta$.

	20°	74·5°	99°	146°	195°	252°	295°	353°
k	0·630	0·871	0·984	1·197	1·423	1·685	1·912	2·179

The association factor varies from 1·133 at 20° to 1·0 at 340°, in agreement with C. Liebenoff, who said: Liquid mercury is an alloy of monatomic and polyatomic mercury mols. in which the former predominate. For the **capillary constant,** G. Quincke gave $a^2=8{\cdot}234$ per sq. mm.; L. Grunmach, 6·09 and 7·39; J. Stöckle, 6·548: and S. W. J. Smith, 6·725. W. D. Harkins and E. H. Grafton measured the adhesion of mercury with organic liquids; and T. Iredale also made observations on this subject. C. A. Reeser and R. Sissingh measured the thickness of surface films of smoke, air, and oil on mercury.

The curious electrocapillary properties of mercury—indicated in **1.** 16, 3—have been the subject of many investigations,[6] and they have been utilized by G. Lippmann[7] and others in the construction of the so-called capillary electrometer, and of the drop-electrometer. K. Wolter measured the electric charge on droplets of mercury at press. of one to nine atm.

The reported values—by N. Kasterin, C. Maltézos, and those indicated in connection with the surface tension—for the **specific cohesion** of mercury vary from $a^2=5{\cdot}8$ per sq. mm. of H. Sentis to 8·51 per sq. mm. of G. Quincke, and the best representative value approximates to 6·75. J. Stöckle gave 6·548 for a^2 against mercury vapour at 15°; G. Quincke, 8·234 against air at 77·5°; G. Meyer, 7·60 at 18° against air; 7·58 against oxygen; 7·58 against nitrogen; 7·33 against carbon dioxide; and 8·33 against hydrogen. M. L. Frankenheim and K. Sondhaus gave for the value of $a^2=4{\cdot}050^2-0{\cdot}00579\theta$, at $\theta°$ between 13·6° and 96·4°; and $a^2=3{\cdot}9782-0{\cdot}00529\theta$ between 107·9° and 116·7°. H. Siedentopf gave 0·000185 for the temp. coeff. of the specific cohesion.

T. Lohnstein, and J. E. Verschaffelt have investigated the theoretical curvature of the **mercury meniscus.** K. Scheel and W. Heuse, J. Palacios, J. E. Verschaffelt, H. Göckel, and L. W. Winkler studied the corrections necessary in allowing for the volume of the meniscus during measurements of volumes, etc. K. Scheel and W. Heuse, and J. Palacios have measured the volume of the mercury meniscus in tubes of different diameter. The results of the latter are indicated in Table III. If a substance under dil. sulphuric acid be brought on a surface of mercury, K. Schaum, and A. Thiel showed that there is a movement in consequence of the electrocapillary action—*vide infra*—and J. Bernstein found that if a crystal of potassium dichromate be in the vicinity of a globule of mercury under nitric acid, there is an irregular change of form in consequence of the oxidation of the mercury on one side and the dissolution of the oxide. S. R. Williams studied the effect of a magnetic field on the meniscus. H. von Euler and G. Zimmerlund studied the effect of the outflow of mercury into a soln. of mercuric nitrate.

E. Villari[8] found that the velocity of flow of mercury from capillary tubes below 0·3 mm. diam., is in general inversely proportional to the length of the tube and proportional to the square of the radius. C. E. Fawsitt stated that the **viscosity** of mercury is nearly twice as great as that of water. G. D. West investigated the motion of a thread of mercury in a glass tube. E. Warburg found that at 17·2°, the viscosity coeff., η, is 0·016021 grm. per cm. per sec.; T. S. Schmidt, 0·01543 at 17·1°; A. Umani, 0·01577 at 10°; E. von Schweidler, 0·01684 at 0°, 0·01609 at 13·5°, 0·01589 at 20°, and 0·01483 at 40°. S. Koch gave:

	−21·4°	0°	10·1°	16·7°	99°	196·7°	282°	340·1°
η . .	0·01868	0·01688	0·01620	0·01575	0·01227	0·01018	0·009499	0·008975

and he represented his observations by $\eta=0{\cdot}016969-0{\cdot}0_4660525\theta+0{\cdot}0_620847\theta^2-0{\cdot}0_92455\theta^3$. K. F. Slotte gave $\eta(1+0{\cdot}00366\theta)=0{\cdot}01693$; and A. Batschinsky, $\eta T=$constant, where T is the absolute temp. M. Plüss, and J. E. P. Wagstaff also measured the viscosity of mercury. According to E. C. Bingham and J. P. Harrison,

the **fluidity**, *i.e.* the reciprocal of the viscosity, is a linear function of the temp. S. Koch gave $\eta=0{\cdot}000622$ for the viscosity of mercury vapour at 370°; 0·000162 at 0°; and at $\theta°$ he obtained $\eta=0{\cdot}000067+0{\cdot}000001155\theta$, between 270° and 380°. These numbers were confirmed by A. A. Noyes and H. M. Goodwin, and H. B. Phillips, and used by O. E. Meyer to calculate the molecular speed and collision frequency of the molecules. M. Knudsen, and S. Weber regard S. Koch's values for the viscosity of mercury as inaccurate. W. C. McC. Lewis gives 12,645 atm. for the **internal pressure** of mercury at 0°. The coeff. of **diffusion** of a number of metals in mercury has been measured. M. von Wogau found for lithium, $k=0{\cdot}66$ (8·2°) per sq. cm. per day; sodium, 0·64 (9·6°); potassium, 0·53 (10·5°); rubidium, 0·46 (7·3°); cæsium, 0·45 (7·3°); calcium, 0·54 (10·2°); strontium, 0·47 (9·4°); barium, 0·52 (7·8°); thallium, 0·87 (11·5°); tin, 1·53 (10·7°); lead, 1·50 (9·4°) and 1·92 (99·2°)—G. Meyer gave 1·37 (15·6°)—zinc, 2·18 (11·5°) and 2·90 (99·2°)—

Table III.—Volumes of Mercury Meniscuses in Cub. mm.

Height in mm.	Radius of tube in mm.						
	5	6	7	8	9	10	11
0·1	4·0	6·5	9·5	13·1	17·2	21·9	27·2
0·2	8·2	13·2	19·3	26·4	34·6	44·0	54·6
0·3	12·5	19·9	29·0	39·8	52·2	66·3	88·2
0·4	17·0	26·8	39·0	53·3	70·0	88·8	110·0
0·5	21·5	33·9	49·1	67·0	87·9	111·0	138·0
0·6	26·2	41·0	59·3	80·9	106·0	134·0	167·0
0·7	31·0	48·3	69·6	94·9	124·0	157·0	195·0
0·8	35·9	55·8	80·1	109·0	143·0	181·0	224·0
0·9	41·0	63·3	90·8	123·0	161·0	204·0	253·0
1·0	46·2	71·0	101·0	138·0	180·0	228·0	282·0
1·1	51·5	78·8	112·0	152·0	199·0	251·0	312·0
1·2	56·9	86·7	123·0	167·0	218·0	276·0	342·0
1·3	62·5	94·8	135·0	182·0	237·0	300·0	372·0
1·4	68·2	103·0	146·0	197·0	257·0	324·0	402·0
1 5	74·0	111·0	157·0	212·0	276·0	349·0	433·0
1·6	79·9	120·0	169·0	228·0	296·0	373·0	463·0
1·7	85·9	128·0	181·0	243·0	316·0	399·0	494·0
1·8	90·1	137·0	193·0	259·0	336·0	424·0	526·0
1·9	—	—	205·0	275·0	356·0	449·0	557·0
2·0	—	—	217·0	291·0	377·0	474·0	589·0
2·1	—	—	—	307·0	397·0	500·0	621·0

G. Meyer gave 2·09 (15°)—cadmium, 1·45 (8·7°) and 2·96 (99·1°)—G. Meyer gave 1·56 (15°)—W. C. Roberts-Austen gave for gold, 0·72 (11°).

S. Koch gave 17,000 cms. per sec. for the **molecular velocity** of mercury vapour at 0°; 344×10^{-8} and 1640×10^{-8} cms. for the **mean free path** respectively at 0° and 300° and atm. press.; and for the **size of the molecules** 67,200 and 14,130 sq. cms. for the total sectional area of all the molecules in 1 c.c. of gas respectively at 0° and 300° and atm. press. K. F. Slotte calculated the edge of the molecular cube of liquid and solid mercury to be $7{\cdot}3\times10^{-9}$ cms. H. S. Hatfield estimated that the radius of an atom is not greater than $1{\cdot}9\times10^{-6}$ cms.; S. Koch, that it is equal to or less than $0{\cdot}19\times10^{-6}$ mm. at 0°; and J. Bernstein, from capillary phenomena, assumed the diameter of the mol. to be $6{\cdot}18\times10^{-7}$ mm. A. Henry calculated a **molecular diameter** $3{\cdot}48\times10^{-8}$ cms. and J. Perrin, $3{\cdot}46\times10^{-8}$ cms. W. Vaubel has made an estimate of the number of atoms in unit vol. A. A. Noyes and H. M. Goodwin say that the mean diameter of the mol. is nearly the same as that of the carbon dioxide mol., and 2·5 times as great as that of the hydrogen molecule. A. Henry calculated $66{\cdot}6\times10^{22}$ for **Avogadro's number**; J. Perrin, $67{\cdot}8\times10^{22}$; and H. Zangger, $62{\cdot}5\times10^{22}$—in the latter case the values ranged

from $5{\cdot}2$–$8{\cdot}7\times10^{23}$. R. C. Dearle, M. Volmer, and A. Terenin made some inferences as to the structure of the atom of mercury. W. R. Fielding said that mercury at its m.p. is more polymerized in the liquid than in the solid state. F. Skaupy found an appreciable dissociation into ions and electrons by metals dissolved in mercury.

J. Dewar [9] found the **breaking stress** of a cast mercury rod 0·2 in. diam. at −182° is 31 lbs.—about half the value for lead at ordinary temp. A. Braun found that solid mercury can be hammered and rolled, and that it is more **ductile** than gold and lead. The **tensile strength** of mercury is the greatest stress per unit area which a column of mercury can support without rupture; thus, if the mercury column is ruptured when it is h cm. longer than the height of the mercury barometer, the tensile strength$=h\times13{\cdot}65\times981$ dynes per sq. cm.—*vide* **1.** 9, 3. The **compressibility** of mercury is smaller than that of any other liquid which has yet been measured. T. W. Richards [10] and co-workers found the coeff. of compressibility, β, between 100 and 500 megabars press., to be 0·00000395 at 20°; P. W. Bridgman found $3{\cdot}79\times10^{-6}$ kgrms. per sq. cm.; W. C. McC. Lewis, $1{\cdot}30\times10^{-6}$ at 20°; H. V. Regnault found $3{\cdot}517\times10^{-6}$; M. Amaury and C. Descamps, $1{\cdot}87\times10^{-6}$; E. H. Amagat, $3{\cdot}92\times10^{-6}$; D. Colladon and C. Sturm, $3{\cdot}4\times10^{-6}$; G. de Metz, $3{\cdot}74\times10^{-6}$; L. Grassi, $2{\cdot}95\times10^{-6}$; P. G. Tait, $3{\cdot}6\times10^{-6}$; C. E. Guillaume, $3{\cdot}9\times10^{-6}$; M. Langlois, $1{\cdot}894\times10^{-6}$; and G. Aimé, $3{\cdot}9\times10^{-6}$ kgrms. per sq. cm. E. Madelung and R. Fuchs gave $3{\cdot}860\times10^{-2}\pm0{\cdot}004$ dynes per sq. cm. Much of this work is inaccurate; J. C. Jamin's results were 50 per cent. too low. In all cases the range of press. was comparatively small. E. H. Amagat, and P. Carnazzi worked up to 3000 atm. L. Troost found that the compressibility of the vapour at about 440°, is very near that of air. P. Carnazzi found that the coeff. of compressibility of mercury at 23° is $3{\cdot}7\times10^{-6}$, and that the coeff. increases as the temp. rises, and for any given temp. diminishes as the press. increases. F. Dolezalek and F. Speidel found for the coeff. $\beta\times10^6$ at different temp. per atm.:

θ	0°	100°	200°	300°	400°	500°
$\beta\times10^6$	3·70	4·17	4·64	5·11	5·58	6·05

and at 24·6° and different press. p, per sq. cm.:

p	92	264	409	532	652
$\beta\times10^6$	4·00	3·97	3·94	3·91	3·01

showing that the dependence of the coeff. on press. is very small. P. W. Bridgman found that at 22°, the changes in vol. δv for press. p up to 12,000 kgrms. per sq. cm. were fairly closely followed by the formula $\delta v=ap+bp^2$, where the constants a and b are obtained from $\log a=4{\cdot}5911-10$; and $\log(-b)=9{\cdot}7782-10$. He gives the results indicated in Table IV and Fig. 2, for the vol. of mercury at different temp. and press. The effects are nearly constant over the entire range of press.; neither the compressibility nor the dilation changes markedly; and the lines bounding the liquid and solid stated are nearly parallel. Consequently, any reversal of the ordinary effects and the appearance of any critical points are outside the range of the diagram. The results resemble those obtained with other compressible liquids. The compressibility and dilation both decrease with rising press.; and, as usual, the effect of rising temp. is to increase the compressibility.

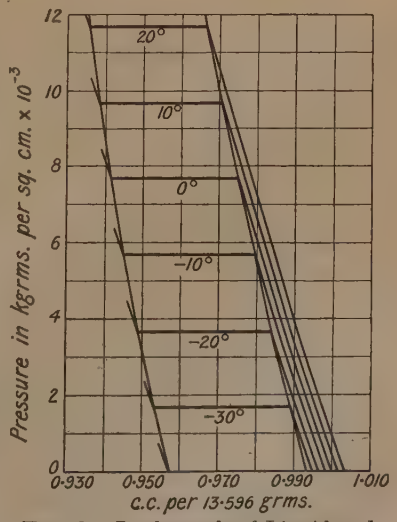

FIG. 2.—Isothermals of Liquid and Solid Mercury.

The **thermal expansion** of mercury was measured by G. D. Fahrenheit [11] in 1672; and by A. L. Lavoisier and P. S. de Laplace in 1781. The former obtained 1·0161 for the volume occupied at 100° by unit vol. of mercury at 0°; and the latter obtained 1·0175. These numbers make the coeff. of thermal expansion respectively 0·000161 and 0·000175. In 1818, P. L. Dulong and A. T. Petit obtained 0·0001802 for the coeff. between 0° and 100°; 0·0001843 between 0° and 200°; and 0·0001887 between 0° and 300°. Since then many observations have been made because an accurate determination of this constant is of importance in the many applications of mercury, and more particularly in thermometry, barometry, etc. In 1847, H. V. Regnault repeated P. L. Dulong and A. T. Petit's work, and obtained the coeff. 0·0001815 between 0° and 100°; 0·0001840 between 0° and 200°; and 0·0001866 between 0° and 300°. He represented the coeff. of cubical expansion, α, at $\theta°$ between 0° and 300°, by $\alpha=0{\cdot}00017905+0{\cdot}00000005504\theta$. J. Bosscha made a critical study of H. V. Regnault's observations. H. Militzer's value $\alpha=0{\cdot}000174$ between 1·5° and 22° is too low. A. Wüllner represented

Table IV.—The Volume of Mercury at Different Temperatures and Pressures.

Pressures in kgrms. per sq. cm.	Volumes in c.c. (vol. of mercury at 0° and 1 atm. = unity).					
	−30°	−20°	−10°	0°	10°	20°
0	0·99457	0·99638	0·99819	1·00000	1·00181	1·00362
1000	99207	99280	99553	0·99626	0·99799	0·99972
2000	98760	98927	99094	99261	99428	99593
3000	—	98581	98743	98905	99067	99232
4000	—	98245	98403	98561	89719	98877
5000	—	—	98077	98231	98385	98540
6000	—	—	97763	97914	98065	98216
7000	—	—	—	97607	97756	97904
8000	—	—	—	—	97461	97608
9000	—	—	—	—	97182	97327
10000	—	—	—	—	96915	97059
11000	—	—	—	—	—	96806
12000	—	—	—	—	—	96567
Change of vol. on freezing	0·03435	0·03418	0·03388	0·03337	0·03243	0·03142
Freezing press.	1740	3710	5670	7640	9620	11600

his results by $\alpha=0{\cdot}0_3181163+0{\cdot}0_7115554\theta+0{\cdot}0_{10}21187\theta^2$; G. Recknagel, by $\alpha=0{\cdot}0_318018+0{\cdot}0_894\theta+0{\cdot}0_{10}5\theta^2$; and H. L. Callendar and H. Moss, their results by $\alpha\times10^{10}=1805553+12444(\theta/100)+2539(\theta/100)^2$—for less exact work, the latter used the linear equation $\alpha=0{\cdot}00018006+0{\cdot}00000002\theta$, and W. E. Ayrton and J. Perry showed that between −39° and 0°, α varies linearly with temp., and M. Thiesen and K. Scheel gave $\alpha\times10^9=(181792+0{\cdot}175\theta+0{\cdot}0351160^2)$. Measurements have also been made by P. de Heen, L. Levy, A. Mahlke, W. Herz, D. I. Mendeléeff, and G. Leonhardt. G. Vicentini and D. Omodei found for the expansion coeff. of the solid metal 0·000179; L. Grunmach gave 0·000123; and J. Dewar gave 0·0000887 for the mean coeff. of cubical expansion between −188° and 17°. H. L. Callendar and H. Moss represented the vol. v, at $\theta°$, by $v=v_0\{1+0{\cdot}000023850+0{\cdot}0000000131(\theta-100)^2\theta\}$; and M. Thiesen, by $v=v_0(1+0{\cdot}0_318182\theta+0{\cdot}0_878\theta^2)$—*vide* sp. gr. K. Scheel and W. Heuse, and N. Eumorfopoulos claimed that the results by H. L. Callendar

and H. Moss are a little low. M. Thiesen and K. Scheel's values for the mean coeff. of thermal expansion of mercury between 0° and 360° are indicated in Table V.

Table V.—Mean Coefficient of Thermal Expansion of Mercury between 0° and 360°.

°C.	$\alpha \times 10^8$									
	0	1	2	3	4	5	6	7	8	9
0	18179	18180	18181	18183	18186	18189	18193	18198	18203	18209
10	18216	18224	18232	18241	18250	18261	18272	18284	18296	18309
20	18323	18338	18353	18369	18396	18403	18421	18440	18469	18480
30	18500	18522	18544	18567	18591	18616	18641	—	—	—

P. W. Bridgman found that the compressibility decreases more rapidly the higher the temp. as shown in Table III; P. Carnazzi's measurements on the effect of press. between 1 and 3000 atm., and temp. between 52·8° and 191·8°, on the coeff. of expansion of mercury, are indicated in Table VI. F. Hoffmann and W. Meissner

Table VI.—Effect of Pressure and Temperature on the Coefficient of Thermal Expansion.

Press. atm.	52·8°	101°	150·3°	191·8°
1	0·0001809	0·0001817	0·0001827	0·0001830
1000	1769	1785	1781	1782
2000	1692	1752	1723	1732
3000	1574	1721	1651	1681

found the mean coeff. of expansion at $\theta°$ and press. p atm. between 100° and 300° to be $181{\cdot}81\times10^{-6}+3{\cdot}47\times10^{-9}\theta+3{\cdot}93\times10^{-11}\theta^2-0{\cdot}2\times10^{-15}\theta^3$; and between 200° and 500°, $\{182{\cdot}22\times10^{-6}+1{\cdot}31\times10^{-9}\theta+3{\cdot}99\times10^{-11}\theta^2+9{\cdot}3\times10^{-15}\theta^3\}\{1-4{\cdot}7\times10^{-9}\theta(p-1)-4{\cdot}7\times10^{-9}(p-1)\}$.

The **thermal conductivity** of mercury was first measured by A. J. Angström[12] in 1864, and he found the absolute conductivity at 50° to be 0·0177 cal. per cm. per sec. per degree. R. Weber found 0·0197 at 25°; A. Berget, 0·02015 between 0° and 100°. Measurements have also been made by A. Berget, and H. R. Nettleton. G. Gehlhoff and F. Neumeier found for the thermal conductivity L between −193° and 149·4°:

	−193°	−78·4°	−37·2°	20·7°	−0°	27·0°	99°	149·4°
L	0·116	0·0776	0·0218	0·0233	0·0248	0·0276	0·0349	0·0385

The results are plotted in Fig. 3. A. W. Porter and F. Simeon found the ratio of the thermal conductivity of mercury in the solid state to that in the liquid state is 3·91. Since the electrical conductivity of mercury decreases with rise of temp., H. Herwig sought if this also applied to the thermal conductivity, and found that the heat conductivity remains constant between 40° and 160°, but this does not appear to be correct. H. F. Weber represented the thermal conductivity λ at $\theta°$ by $\lambda=0{\cdot}01479+0{\cdot}000083\theta$. A. Berget obtained a negative temp. coeff. −0·001267 between 0° and 100°, and −0·00045 between 0° and 300°, in accord with G. Wiedemann and R. Franz's rule. A. Hirschi found indications of a change in the thermal conductivity when an electric current is

passing through mercury. A. Schleiermacher reported the thermal conductivity of mercury vapour at 203° to be 0·00001846, and to be independent of variations of press. of 3 to 10 mm., and the temp. coeff. is 0·0074.

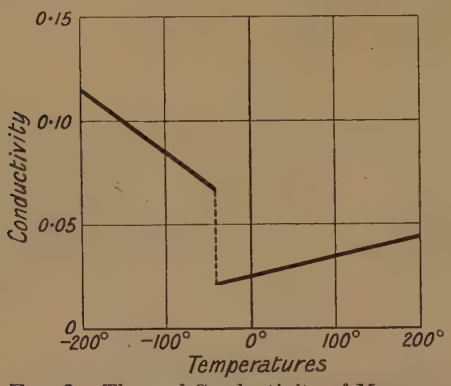

FIG. 3.—Thermal Conductivity of Mercury —Solid and Liquid.

P. L. Dulong and A. T. Petit[13] found the **specific heat** of mercury between 0° and 100° to be 0·0330, and between 0° and 300°, 0·0350; H. V. Regnault found 0·0282 between 5° and 16°; 0·0283 between 10° and 15°; and 0·0290 between 15° and 20°. H. V. Regnault's values are too small, and P. L. Dulong and A. T. Petit's conclusion that the sp. ht. of mercury increases with a rise of *temperature* is not in agreement with later observations. According to A. Winkelmann, the sp. ht. of mercury, unlike that of many other liquids, decreases with a rise of temp., and he represented his results at $\theta°$ between 19° and 142°, by $c=0{\cdot}03336-0{\cdot}0000069\theta$. O. Petterson found $c=0{\cdot}033266-0{\cdot}0000092\theta$; and A. Naccari, found $c=0{\cdot}033277-0{\cdot}0000053432(\theta-17)+0{\cdot}000000001667(\theta-17)^2$ between 12° and 228°. H. T. Barnes and H. L. Cooke obtained $c=0{\cdot}033458-0{\cdot}00001074\theta+0{\cdot}00000003850\theta^2$ between 3° and 84°. The mean values of A. Winkelmann's, A. Naccari's, and J. Milthaler's determinations are :

	0°	20°	40°	60°	80°	100°	140°	180°	200°
c .	0·03333	0·03319	0·03304	0·03290	0·03276	0·03262	0·03233	0·03203	0·03189

A. Naccari obtained 0·03235 at 200°, 0·03226 at 220°, and 0·03217 at 240°. W. J. Kurbatoff found the mean sp. ht. between 0° and 306° to be 0·0325 to 0·0331, which is much smaller than the result—0·03731—which he obtained six years earlier. H. T. Barnes and H. L. Cooke's value for C_p at 0° is 0·03346 gram-cal. per gram, or 0·4549 gram-cal. per c.c. F. Simon gave $C_p=2{\cdot}252$ at 18·7° K., and 6·863 at 231·8° K.

The ratio of the sp. ht. of liquid mercury at θ to that at 0° shows the same results another way. The mean values of A. Bartoli and E. Stracciati's, A. Winkelmann's, and H. T. Barnes and H. L. Cooke's observations are :

C_{20}/C_0	C_{30}/C_0	C_{40}/C_0	C_{80}/C_0	C_{80}/C_0
0·9957	0·9933	0·9903	0·9863	0·9826

F. Koref obtained 0·0334 for the sp. ht. of liquid mercury between —35·6° and 3·4°. H. V. Regnault found the sp. ht. of solid mercury between —78° and —40° to be 0·03192; and therefore, like other substances, the sp. ht. of mercury is greater in the liquid than in the solid state :

	Water.	Lead.	Mercury.	Sulphur.	Calcium chloride (hydrated).
Solid . .	0·502	0·0314	0·03192	0·2026	0·345
Liquid. .	1·000	0·0402	0·03330	0·2340	0·555

P. Nordmeyer and A. L. Bernoulli found 0·0324 for the sp. ht. of mercury between —185° and 20°; F. Koref, 0·0329 between —77·2° and —41·8°; H. Barschall, 0·0320 between —183·3° and —71°; J. Dewar, 0·0232 at —223°; and F. Pollitzer found for the sp. ht., c, and for the **atomic heat** :

	—211·5°	—204°	—183°	—64°	—40°	—37°	—30°
c . .	0·02670	0·02715	0·028275	0·03260	0·03475	0·03490*	0·03545*
At. ht. .	5·340	5·430	5·695	6·520	6·950	6·98*	7·09*

The numbers with the asterisk refer to liquid mercury, the others to the solid. Other observations have been made by M. Langlois, F. Weber, J. N. Brönsted, A. S. Russell, and C. Cantoni. According to A. Eucken, the at. ht. for liquid mercury at 0° is C_v=5·9, and C_p=6·7; at 160°, C_p=6·59; and at 260°, C_p=6·63; for solid mercury at −40°, C_v=5·95, and C_p=6·7. Above the m.p. the sp. ht. of mercury has thus a negative temp. coeff. as H, T. Barnes has shown. E. Heilborn deduced for an element with monatomic molecules the relation between the sp. ht. and temp., the expression $c=c_0v^{-\frac{1}{3}}$, where v denotes the sp. vol. which can be calculated for liquid mercury from J. Bosscha's formula, or the observed values can be used; and c_0=0·033412, the sp. ht. at 0°. The agreement between the observed and calculated values is satisfactory. L. Sohncke applied E. Heilborn's formula to other metals. P. W. Bridgman calculated values for the difference of the two sp. ht. of mercury, C_p-C_v, from (27), **2**. 13, 1—and made observations on the influence of press. on the vol. of mercury; and he likewise calculated the influence of *pressure* on the sp. ht. of mercury from the thermodynamic relation $(dC_p/dp)_v=-T(d^2v/dT^2)_p$; with C_p expressed in ergs per c.c., and p in dynes, $(dC_p/dp)_v=-0{\cdot}00000655$; and with Cp in gram-cals. and p in kgrms. per c.c., −0·000000154. This variation is small, and corresponds with about ¼ per cent. for 7000 kgrms. Expressing the press., p, in kgrms. per c.c., and the sp. ht. in gram-cals. for initially unit vol. (13·596 grms.), the values of C_p and C_v at 0° are:

p	0	1000	2000	3000	4000	5000	6000	7000
C_p	0·4549	0·4547	0·4546	0·4544	0·4543	0·4541	0·4540	0·4538
C_v	0·4003	0·4035	0·4056	0·4063	0·4073	0·4073	0·4077	0·4079

Hence, while C_p decreases with an increase of press., C_v increases, and the increase is more rapid than the decrease. According to F. Richarz, the sp. ht. of solid mercury is about four times as great as when the mercury is in the gaseous state. A. Kundt and E. Warburg found the sp. gr. of mercury vapour at constant vol. to be 0·1027, and at constant press. 0·0245; and the ratio of the two sp. hts. to be 1·666. R. C. Tolman gave 41·1 for the **entropy** of mercury at 25°. G. N. Lewis and co-workers found 41·51 (gas), 17·8 (liquid).

The freezing of mercury was first reported by J. A. Braun,[14] in 1760, and discussed in his paper: *De admirando frigore artificiali quo mercurius seu hydrargyrus est congelatus*. H. Cavendish gave −39·38° for the **melting point** or rather the f.p.; T. Hutchins, −39·44°; H. V. Regnault, −38·5°; G. G. Person, −39°; G. Quincke, −40°; J. Timmermans, −38·65°; F. Henning, −38·89°; F. G. Keyes and co-workers, −38·90°; K. Scheel, −38·89; and G. K. Burgess, −38·7°, with an uncertainty of about 0·1°. A. Marcet made some observations on this subject. W. Guertler and M. Pirani give −39·7° as the best representative value. According to G. Tammann, the m.p. is raised 0·0054° per kgrm. *pressure* per sq. cm. P. W. Bridgman found the f.p. of mercury under various press. p in kgrms. per sq. cm.:

	−19·9°	−9·8°	0·00°	9·16°	12·88°	16·4°	18·45°
p	3660	5590	7570	9450	10140	10910	11350

The change in volume which occurs when mercury freezes was observed by W. E. Ayrton and J. Perry. G. Vicentini and D. Omodei found there is over a five per cent. expansion when mercury changes from the solid to the liquid state, for 1 c.c. becomes 1·05098 c.c. J. W. Mallet found 3·7 per cent.; and L. Grunmach found that unit vol. of solid mercury becomes 1·050982 vols. in the liquid state so that the expansion is over 5 per cent. P. W. Bridgman measured the change in vol.—δv c.c. per gram—which occurs when mercury freezes at different press. —p kgrms. per sq. mm.:

	−19·9°	−9·8°	0°	5·23°	9·16°	16·40°
p	3660	5590	7570	8660	9450	10910
δv	0·002515	0·002492	0·002454	0·002426	0·002399	0·002348

M. Lémeray has made observations on the relation of the m.p. to the coeff. of expansion; and H. Ramage compared the m.p. of mercury with that of other elements. M. Faraday [15] showed vapour arises from mercury both in vacuo and in spaces filled with air, as shown by the "silvering" of gold-leaf kept for two months confined over mercury; consequently, "at common temp., even in the presence of air, mercury is always surrounded by an atm. of the same substance." C. W. Easley, J. W. Mallet, W. T. Burgess, E. Bindschedler, J. Davy, and M. Berthelot noted the **volatilization of mercury** at ordinary temp. by the formation of mercuric iodide about the necks of bottles containing iodine and situated some yards away from the mercury. C. J. B. Karsten found that a photographic plate, held over mercury below 0°, is affected by the vapour of that element. C. Brame claimed that the finely divided *utricules de soufre*, obtained when sulphur is condensed from the vapour, furnish a more delicate test for mercury vapour than gold-leaf. He thus showed that at 12°, mercury vapour rises above a metre, and even at 8°, it has no limited atm.; and at ordinary temp., mercury vapour rises from amalgams and mercurial ointments.

According to W. Burnett, some mercury, forming part of the cargo of a ship on the Spanish coast, ran out of the bladders which had become rotten, and found its way into the hold, where it mixed with the bilge-water. As a result, every piece of metal in the vessel was coated with mercury, and the whole ship's company was affected with violent symptoms of salivation.

G. G. Stokes, and C. Brame made observations on the diffusion of mercury vapour; the latter found that in the presence of sulphur vapour and air, mercury vapour diffuses in accord with the same law as other gases, but in the presence of iodine vapour and air, and of the mercuric iodide vapour thereby produced, the law of diffusion appears to be different. W. F. Reid observed the volatilization of mercury exposed to the sunlight, and H. V. Regnault noted the volatilization of mercury at −13°. A. Merget found that the volatilization is not arrested by freezing the mercury, and he noticed that it occurred at −44°; and C. J. Hansen noted the metal volatilized in vacuo at −40°. R. F. Howard suggested that fine globules of mercury are more volatile than a large bead of the same element—1. 10, 1. F. Glaser measured the loss which occurs with electrolytic mercury per sq. cm. of surface per hour, and found 0·002 mgrm. was lost at room temp., 0·010 mgrm. in a desiccator over sulphuric acid; and 0·016 to 0·727 mgrm. as the temp. rose from 30° to 100°. V. Borelli observed a loss when mercury is confined in a desiccator over sulphuric acid, but not over potassium hydroxide. J. D. van der Plaats observed the volatilization of mercury confined in an atm. of carbon dioxide and nitrogen. K. Bennewitz measured the **rate of evaporation** of mercury in vacuo. The subject was also studied by M. Volmer and I. Estermann between 59° and −180°. E. Rie computed that mercury droplets of radius 10^{-5} cm. can distil into the larger drops. C. Barfoed noted that mercury can evaporate at ordinary temp. through a layer of water. J. W. Mallet, M. T. Lecco, and S. Hada found mercury distils over with water, and collects in the receiver. F. W. Dafert found the volatilization of mercury is prevented by covering it with glycerol, but not by water or by mineral oil. C. Barreswil stated that the presence of a little platinum accelerates the volatilization of mercury. R. W. Wood found that mercury condensed as a continuous film on glass cooled to −150°, but not at −130°, so that the critical temp. has some intermediate value.

Numerous observations have been made on the **vapour pressure**, p, of mercury; and the results are not always concordant. Very few seem to have regarded the degree of purity of the mercury as a factor of any particular importance. M. Knudsen found:

	0°	7·1°	19·6°	30·2°	39·8°	46·2°	50·8°
p (mm.)	0·0001846	0·0003677	0·001138	0·002806	0·005966	0·009599	0·01331

H. Hertz found:

	60°	80°	100°	120°	140°	160°	180°	200°
p (mm.) . .	0·026	0·093	0·285	0·779	1·93	4·38	9·23	18·25

S. Young found the following values of p, and A. Smith and A. W. C. Menzies the values of p' :

	128°	150°	200°	300°	350°	400°	450°	480°
p (cm.) . .	—	—	1·681	24·86	67·25	154·85	315·05	459·6
p' (cm.) . .	0·0829	0·0802	—	24·585	66·977	156·61	324·50	—

L. P. Cailletet, E. Colardeau, and A. Rivière gave :

	450°	500°	550°	600°	650°	700°	750°	880°
p (atm.) . .	4·25	8·0	13·8	22·3	34·0	40·0	72·0	162·0

Measurements have been made by T. E. Thorpe between 2·1° and 19·9° ; by E. Hagen between 0° and 100° ; by O. Ruff and B. Bergdahl between 205° and 357° ; by H. V. Regnault between 0° and 520°—but C. Barfoed said that these results are too high ; by H. Hertz between 0° and 220°—and discussed by C. von Rechenberg ; by W. Ramsay and S. Young between 40° and 520° ; by T. H. Laby between 255° and 450° ; by E. W. Morley between 16° and 60° ; by L. Pfaundler between 15° and 98·8° ; by F. B. Jewett between 140° and 300° ; by L. A. Gebhardt between 130° and 310° ; and by A. Villiers between 60° and 100° in atm. of hydrogen and of carbon dioxide. J. Juhlin, Lord Rayleigh, F. A. Henglein, C. F. Hill, J. Dewar, H. McLeod, P. de Heen, and T. Ihmori, have also made observations on this subject. J. D. van der Plaats found the vap. press. of mercury in carbon dioxide at 0° is 0·0047 mm. ; at 10°, 0·008 mm. ; and at 20°, 0·013 mm. A. Smith and A. W. C. Menzies worked between 253·97° and 434·71°, and they calculated a table for every 2° for the vap. press. of mercury between 0° and 450° from the formula : $\log p=9·9073436-3276·628\theta^{-1}-0·6519904 \log \theta$, which represents the observed results very satisfactorily between 120° and 453°. H. V. Regnault represented the vap. press. p mm. of mercury at $\theta°$ by $\log p=0·6640459-7·7449870a^{\theta}+0·3819711b^{\theta}$; C. Antoine, by $\log p=4·2520(2·0323-1000/t)$, where $t=\theta+380$; F. A. Henglein, by $\log p=7·5030-1295·9/T^{-1·0605}$ mm. ; and A. Jarolimek, by $\theta=175+190·5p^{0·25}-8p^{-1}$. T. H. Laby represented his results between 15° and 270° by $\log_{10}p=15·24431-3622·932T^{-1}-2·367233 \log_{10}T$, and between 270° and 450° by $\log_{10}p=10·04087-3271·245T^{-1}-0·7020537 \log_{10}T$; M. Knudsen found $\log_{10}p=10·5724-3342·26T^{-1}-0·847_{10}T$ to be very exact near 50°, but less satisfactory at higher temp. ; and A. C. Egerton gave $p=3·72 \times 10^{13}T^{\frac{1}{2}}e^{-160\times10^4/RT}$ dynes per sq. cm.

The **boiling point** of mercury was stated to be 346·5° by J. Crichton ; 349°, by J. Dalton ; 339°–359°, by T. Carnelley and W. C. Williams ; 350°, by R. Pictet, P. H. van der Weyde, and by L. Troost ; 355°, by V. Meyer and J. M. Crafts ; 357°, by O. Ruff and B. Bergdahl ; 356·25°, by P. Heinrich ; 356·7°, by H. L. Callendar ; 357·25°, by H. V. Regnault ; 357·3°, by J. M. Crafts ; 357·65°, by E. H. Griffiths ; 356·76°, by H. L. Callendar and E. H. Griffiths ; 356·95°, by A. Smith and A. W. C. Menzies (sulphur b.p.=445°) ; 360°, by P. L. Dulong and A. T. Petit, and H. St. C. Deville ; 357° at 760 mm., and 310° at 33 mm. press., by P. de Heen ; 365° at 760 mm. and 155° in vacuo, by C. J. Hausen. F. Krafft and P. Lehmann found mercury to boil in the cathode vacuum at 174° when the press. was 195 mm. H. V. Regnault calculated the b.p. of mercury to be :

p (mm.) . .	720	730	740	750	760	770	780
B.p. . . .	354·3°	355·0°	355·8°	356·5°	357·25°	358·0°	358·8°

The best representative value is 357·01° when the b.p. of sulphur 445° is taken as the standard of reference. According to H. C. Dickinson, to prevent the boiling of mercury in a thermometer, the space above it should be filled with some dry, inert gas, such as nitrogen or carbon dioxide, having a press. of one atm. at 300°, 4·5 atm. at 450°, and 20 atm. at 550°. L. H. Borgström gave 790° for the b.p. of mercury at 93 atm. press.

T. H. Laby estimated the **critical temperature** of mercury to be over 800°; I. Traube and G. Teichner, and C. M. Guldberg, over 1000°; S. Weber, 1450°; and H. Rassow, over 1400°. W. J. Kurbatoff assumed that the critical temp. must be high because of the simplicity of the molecule of mercury. H. Happel gave 1370° for the critical temp., and 456 atm. for the **critical pressure**. S. Weber gave 1042° for the critical temp. J. Königsberger gave 1270° as an approximation to the critical temp. in a quartz glass capillary tube; and 1000 atm. for the critical press. From the curves of the densities of liquid and vapour, Fig. 4, the critical temp. appears to lie between 1500° and 1600°. The critical press. is probably near 2000 atm. G. Meyer computed 1474°. E. Ariès estimated respectively 1350° and 420 atm.; and J. J. van Laar, 1172° and 179 atm. with 3·3 for the **critical density.**

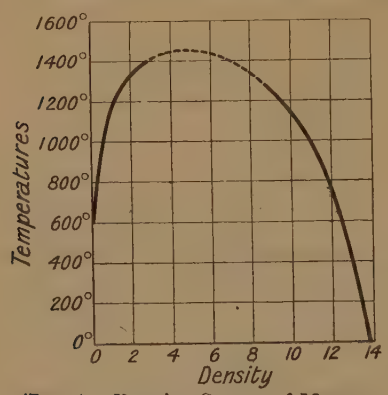

FIG. 4.—Density Curves of Mercury —Vapour and Liquid.

S. Weber gave 5·0 for the critical density. A. W. C. Menzies found that the liquid phase vanishes in a sealed quartz glass tube at about 1275° when the vap. press. of the mercury is about 675 atm. (the press. of the air in tube was 0·03 mm.). J. Bender and J. Königsberger determined the sp. gr. of liquid mercury and the density of its sat. vapour at different temp. The corresponding curve is shown in Fig. 4, where the critical temp. is near to 1430°, or 1703° K.; the critical press. is 1042 atm., and the critical density 5·0. These numbers were shown by S. Weber to be in agreement with R. Eötvös' rule, J. D. van der Waals' equation, and F. Trouton's constant calculated by I. W. Cederberg's formula:

$$\frac{\lambda M}{T}\left(1-\frac{T}{T_c}\right)=4{\cdot}57\left(1-\frac{1}{p_c}\right)\log p_c$$

with W. J. Kurbatoff's value for the latent heat $\lambda=67{\cdot}8°$ K. M. Prud'homme, and E. van Aubel discussed the relation between the critical temp., the b.p., and the m.p. of mercury.

According to G. G. Person,[16] the **heat of fusion** of mercury is 600 cals. per gram-atom, or 2·84 cals. per gram at the m.p.; F. Pollitzer gave 554·5 cals. per gram-atom or 2·75 cals. per gram at −38·7°; F. Koref gave 571 cals. per gram-atom, or 2·855 cals. per gram; and M. Langlois gave 2·836 cals. per gram. A. C. Egerton calculated the mol. ht. of fusion of mercury to be $5{\cdot}6\times10^2$ cals. at the m.p. P. W. Bridgman calculates for the change of latent heat on freezing mercury:

	−40°	−30°	−20°	−10°	0°	10°	20°	
v	0·002535	0·002526	0·002515	0·002492	0·002454	0·002393	0·002311	c.c. per grm.
$dp/d\theta$	196400	196500	196600	196900	197600	198350	0·199300	grm. per sq. cm.
Latent heat	2·720	2·828	2·939	3·025	3·103	3·149	3·163	cals. per grm.

and for the change in the internal energy of mercury in passing from the liquid to the solid state:

	−28·66°	−18·48°	−8·31°	1·87°	12·06°	22·24°	
p	2000	4002	6005	8018	100034	12064	kgrms. per sq. cm.
Work, $p\delta v$	0·118	0·235	0·350	0·459	0·557	0·649	gram-cal.
Energy change	2·732	2·717	2·693	2·657	2·599	2·516	cals. per grm.
Latent heat	2·848	2·951	3·041	3·114	3·154	3·165	

The **heat of vaporization** at 623° was found by G. G. Person to be 62 cals. per

gram or 12·4 cals. per gram-atom; W. J. Kurbatoff gave 67·8 cals. per gram, or 13·6 cals. per gram; M. Knudsen, 71 cals. per gram; M. Langlois, 77 cals. per gram; C. Musceleanu, 63·66 cals. per gram at 2×10^{-3} mm. press.; and D. Konowaloff, and J. C. G. de Marignac, 15·5 Cals. per gram-atom. W. C. McC. Lewis estimated the latent heat of vaporization at 0° to be 6·26 Cals. per gram-atom, or 31·28 cals. per gram; and at 20°, 6·34 Cals. per gram-atom, or 31·71 cals. per gram. K. K. Järvinen calculated a value from the theory of mol. attraction. A. C. Egerton gave $1·57\times10^4$ cals. for the **heat of sublimation** of the solid. According to W. J. Kurbatoff, **Trouton's constant** is 21·5, so that the liquid is not associated at the b.p.; C. Musceleanu found 19 to 23; and E. van Aubel, 20. R. de Forcrand found when the latent heat of vaporization is 13·945 Cals. per gram-atom, and the b.p. T=630 K., λ/T=10·1 log T−1·5−0·009T+0·0000026T^2, or 22·135. P. dc Heen has discussed the relations between the saturated vapour and Trouton's rule; J. P. Montgomery, the relations between several constants, and Trouton's rule; W. Vaubel gave the **heat of dissociation**, Hg_2=2Hg−446 Cals.; C. Cantoni, the **heat of disaggregation** of the molecules of the liquid; and C. Cantoni, and W. C. McC. Lewis, the latent **heat of expansion** of the liquid against the external press.—the latter gives 13280 atm. per sq. cm. or 316 cals. per c.c. E. Beckmann and O. Liesche gave 114·0 for the **boiling constant** of mercury. W. G. Duffield gave $9·4\times10^4$ to $11·5\times10^4$ cm. per sec. for the velocity of the mols. projected from boiling mercury. G. Bakker calculated the energy transformation between the capillary film of the liquid and the vapour. I. Langmuir has studied the consumption of electrical energy necessary to maintain the temp. of a tungsten wire in mercury vapour. O. Sackur obtained for the chemical constant $\mathbf{C}$=−2·055+1·5 log M, where M is the mol. wt.

The **index of refraction**, μ, of liquid mercury; and the **absorption coefficient**, k, such that the amplitude of a wave after travelling one wave-length, λ, in the metal, is reduced in the ratio $1:e^{-2\pi k}$ have been measured by W. Meier,[17] who found:

λ	325·4	361·1	398·2	441·3	467·8	508·0	589·3	630·0
μ	0·679	0·774	0·921	1·011	1·149	1·312	1·624	1·719
k	3·323	3·510	3·438	3·387	3·207	2·986	2·713	2·733

E. van Aubel found μ=2·30 for the H_α-line. P. Drude obtained for λ=589·3, μ=1·73, and k=2·87. W. von Uljanin has also measured the index of refraction and absorption coeff. of liquid mercury. R. W. and R. C. Duncan found for light of wave-length 665·0, 589·3, and 472·0 the respective indices of refraction 2·34, 1·92, and 1·35; and absorption coeff. 2·47, 2·78, and 3·42. C. Cuthbertson found the refractive index of the vapour of mercury to be 1·001857, and C. Cuthbertson and E. P. Metcalfe found for the wave-lengths 656·2, 598·3, 545·9, and 518·3, the respective values 1·001799, 1·001866, 1·001882, 1·001885; and for the visible rays, $\mu-1=0·001755(1+2·265)$ $0·001755(1+2·265\lambda^{-2}10^{-10})$. The rate of change is thus about four times as great as with air; and J. C. McLennan gave:

λ	4860	5132	6110	6230	6234·31
μ	1·000949	1·00943	1·000924	1·000882	1·000860

L. Natanson also measured the index of refraction of mercury vapour. T. des Coudres, and L. P. Wheeler measured the index of refraction of liquids—water, alcohol, hydrochloric acid, sodium thiosulphate soln., petroleum, chloroform, olive oil, turpentine, and carbon disulphide—by reflexion of light from the surface of mercury immersed in the liquid. P. Drude, and W. Meier measured the percentage **reflecting power** of mercury; the latter found for λ=326, 441, 589, and 668, the respective values 66, 74, 75, and 77 per cent. H. Rubens and E. Ladenburg measured the reflecting power for long waves; R. W. Wood, the selective reflexion of monochromatic light by mercury vapour; and P. P. Koch and W. Friedrich, and

B. O'Brien and L. P. Wheeler, the anomalous **dispersion** of mercury vapour. R. W. Wood, and A. von Malinowsky studied the resonance radiation of mercury vapour; the former found that mercury vapour reflects light of wave-length 2536 in much the same way as would a coating of silver inside the bulb. S. Procopiu found the birefringence of toluene is positive, but negative when mercury is shaken therewith. Similarly with benzene, etc. R. W. Wood studied the selective reflection, and the polarized **resonance radiation** of mercury vapour, and Lord Rayleigh, the polarization of light scattered by mercury vapour. M. Tiffeneau and C. Sommaire gave 12·848 for the **atomic refraction** of mercury.

W. N. Hartley,[18] and R. W. Wood observed that a bluish-green **fluorescence** appears when sparks from zinc or cadmium, or cadmium-lead electrodes passed through mercury vapour; the fluorescence gradually decreases in intensity with rise of temp., and finally vanishes altogether, and the phenomenon recurs in the reverse order as the vapour is cooled. E. Paterno and A. Mazzucchelli obtained no fluorescence at 1500° in a quartz tube. J. Franck and R. W. Wood observed that the phenomenon is sensitive to the presence of electronegative gases—oxygen eq. to 3 mm. press. prevents the fluorescence; helium has no appreciable influence. J. N. Collie found all gases luminesce when shaken with mercury. The phenomenon has been studied by W. Steubing, W. Wein, J. H. Vincent, J. S. van der Lingen, W. Matthies, J. Königsberger, A. Perot and J. Bosler, A. Pflüger, R. Pohl, A. Klages, G. C. Schmidt, J. von Kowalsky, F. W. Aston, B. Reismann, F. S. Phillips, Y. T. Yao, G. Cario, etc. O. Wolff found no fluorescence in ultra-violet light. The luminosity which occurs in many gases when an electric discharge is passed through the gas, and persists for some time after the discharge has ceased, has been traced to the readjustment of chemical equilibrium upset by the discharge —oxygen, and nitrogen. N. H. Ricker attributed the phenomenon with mercury vapour to the recombination of positive and negative ions to form neutral mols. N. H. Ricker studied the after-glow or **luminescence** of mercury vapour distilled from an arc in vacuo. The luminescence is attributed to the recombination of the positive and negative ions produced by the discharge as suggested by C. D. Child. The last-named obtained a continuous spectrum with mercury between 120° and 400°, and at a low current density. J. S. van der Lingen studied the fluorescence of mercury vapour excited by X-rays.

The action of **radium radiations** on mercury have been studied by G. le Bon, A. S. Russell, T. S. Taylor, K. Siegl, H. Greinacher, etc. J. Stark and co-workers studied the action of the **cathode rays** on mercury; and S. Landau and H. Piwnikiewicz, the action of **X-rays**. A. Müller studied the high frequency or X-ray spectrum of mercury. In general, the fluorescence increases with increasing vapour density; the temp. has no influence on the intensity of the glow; but the glow is diminished when foreign gases are present; and the spectrum is continuous. M. de Broglie, and W. Duane and co-workers studied the critical absorption of X-rays of wave-lengths $\lambda \times 10^8$ cms. by mercury, and found respectively 0·146, 0·1479, and 0·1491. H. J. C. Ireton attempted to find if mercury atoms emit radiations of wave-length 5460·97 and 4046·78 A. when they have been made to absorb light of wave-length 2536·72 and 4358·66 A., and found evidence to support the hypothesis. The phosphorescence caused by **canal rays** was investigated by J. Königsberger and J. Kutschewsky, W. Wien, A. Rüttenauer, J. Stark, etc. R. de J. F. Struthers and J. E. Marsh found purified mercury had no action whatever on a gelatine dry plate; N. Piltschikoff found no sign of the emission of the so-called Moser rays of mercury. W. Steubing showed that the vapour of mercury is ionized by the light from a mercury lamp. The current was 10^{-8} amps. when the press. was zero. This represented the **photo-electric effect** at the electrodes. The vap. press. of the mercury was increased by heat, and the current rose to a maximum of 6×10^{-8} amps. The current increased almost linearly with the potential difference up to 12 volts, the maximum employed. J. G. Popesco studied the relation between the surface tension and the photo-electric effect.

W. J. Russell, R. Liesegang, A. Colson, J. H. Vincent, and H. Muraoko and M. Kasuya studied the action of mercury on **photographic plates.**

It is generally stated that mercury gives no **flame spectrum.** A. Mitscherlich [19] noticed that mercury cyanide, in the oxyhydrogen flame, furnished the spectral lines 546·0 and 435·8, and G. D. Liveing and J. Dewar observed the line 253·6 with mercury cyanide in the cyanogen flame, but A. Gouy observed no lines with mercuric salt soln. sprayed in Bunsen's flame; W. N. Hartley and H. Ramage observed neither lines nor bands when mercuric oxide is heated in the oxyhydrogen flame; C. de Watteville none with mercuric oxide or chloride in the oxycoal-gas or oxyhydrogen flame; G. D. Liveing and J. Dewar none during the explosion of electrolytic gas; and A. S. King none by heating mercury in the electric furnace. E. Goldstein observed no lines in the spectrum of mercury diphenyl. C. de Watteville did obtain the 253·672 line with mercuric nitrate, acetate, and cyanide. G. D. Liveing has also investigated this subject. C. Wheatstone first reported seven lines in the **spark spectrum** of mercury in air, under reduced press., or under water. D. Alter, A. Masson, A. J. Angström, J. Plücker, F. Brasack, G. Kirchhoff, T. R. Robinson, W. A. Miller, W. Huggins, R. Thalén, J. Plücker and J. W. Hittorf, W. N. Hartley, A. F. Sundell, J. S. Ames, E. Demarçay, A. Schuster and G. Hemsalech, P. G. Nutting, H. E. Watson, H. Finger, E. Castelli, G. Wendt, J. de Kowalsky, etc., made observations on this subject. The principal lines in the spark spectrum from a soln. of mercuric chloride are a feeble line of wave-length 615·2$\mu\mu$ in the orange-yellow; a yellow double line, 53·0 and 53·7, on the scale, or 579·0 and 576·9$\mu\mu$—γ, Fig. 5; feeble yellowish-green lines, 567·8 and

Fig. 5.—Spark Spectrum of Mercury.

559·5$\mu\mu$; an intense green line, 546·1$\mu\mu$, Fig. 5—almost in the same place as one of the silver lines; a feeble blue line, 491·6$\mu\mu$; a stronger indigo-blue line, 126·4, on the scale, or of wave-length 435·8$\mu\mu$, Fig. 5; and two feeble violet lines, 407·8 and 404·7$\mu\mu$. The spark spectrum of mercuric nitrate is not so intense as the spectrum from mercuric chloride; a highly exhausted vacuum tube containing mercury, or the light from an arc between the mercury electrodes of a mercury lamp, gives a similar spectrum. According to E. Cappel, the sensitiveness of the spectrum of mercury in the induction spark is half that of copper, and about $\frac{1}{10000}$th part of mercury can be detected. If the electric discharge is passed through hot mercury vapour not far from its point of condensation, and the current density is small, a **continuous spectrum** ranging from the red to the ultra-violet, and very prominent in the green, is produced. As the current density increases the **line spectrum** becomes more and more prominent, and the continuous spectrum less so. With a condenser in circuit, the line spectrum alone is produced. C. D. Child showed that the glow at the cathode gives the line spectrum more prominently than that of the anode, and that the continuous spectrum does not depend on the kind of glass, the kind of electrodes used, nor on the purity of the mercury. The **fluorescent or resonance spectrum** of mercury vapour was studied by J. S. van der Lingen, R. W. Wood, and E. P. Metcalfe and B. Venkatesachar. J. Franck concluded that the number of rayless transformations in the collision of excited atoms, with slow-moving atoms, is not small compared with unity. The **arc spectrum** of mercury has been studied by H. Kayser and C. Runge, F. M. Walters, A. L. Hughes, H. Buisson and C. Fabry, G. Wiedemann, L. Arons, C. Fabry and A. Perot, O. Lummer, F. Exner and E. Haschek, R. Küch and T. Retschinsky, S. Procopiu, A. Pflüger, etc. C. Ramsauer and F. Wolf studied the duration of the spectral lines in an extinguished arc. S. Procopiu studied the variation in

the arc spectrum with the conditions under which it is formed. By sparking a soln. of the chloride L. de Boisbaudran obtained a **band spectrum** between 659·7 and 549·8, and between 529·2 and 522·2, but it is not known whether these belong to the metal or to the chloride. Observations on the band spectra of mercury and its compounds have been made by E. Wiedemann and C. G. Schmidt, B. O. Pierce, A. C. Jones, H. Nagaoka, E. Hulthén, A. Kratzer, G. Ciamician, H. W. Vogel, E. Gehrcke and L. C. Glaser, A. Kalähne, W. B. Huff, E. Liese, A. Hagenbach and H. Konen, J. Stark and co-workers, J. M. Eder and E. Valenta, J. Lohnmeyer, O. Lummer, etc. According to J. Lohnmeyer, the band spectra of the mercury halides are very complicated, and this the more the greater the at. wt. of the contained halogen. J. N. Lockyer found that mercury vapour gives no visible **absorption spectrum.** J. C. McLennan and W. W. Shaver photographed the spectrum of mercury vapour up to λ=11137 A.; they found that non-luminous mercury vapour does not absorb radiation of λ=10140 A.; but very slight deposits of mercury on the walls of the vessel may give an absorption; radiation of λ=10140 A. may be strongly absorbed by luminous mercury vapour. Hence, from the absence of absorption of radiation λ=10140 A. by non-luminous mercury vapour, the resonance potential of 1·26 volts does not apply to the atoms of mercury in their ordinary state, in addition to the well-established one of 4·9 volts corresponding with λ=2536·72. The selective absorption of light by electrically luminescent mercury vapour has been studied by E. P. Metcalfe and B. Venkatesachar; and A. Terenin shows the bearing of the absorption spectrum on the structure of the mercury atom. R. J. Strutt, R. W. Wood, W. N. Hartley, C. R. Crymble, T. W. Case, J. J. Dobbie and J. J. Fox, H. Ley and W. Fischer, J. Frank and W. Grotrian, R. Küch and T. Retschinsky, etc., made further observations on the absorption of light by mercury vapour. R. C. Dearle measured the infra-red radiation spectrum of mercury. J. C. McLennan, D. S. Ainslie, and F. M. Cale studied the absorption of the λ=5460·97 A. by mercury vapour, F. H. Newman studied the relative visibility of the spectra of mercury and the alkali metals.

A. S. King studied the causes of the variability of the spark spectra of mercury. G. Ciamician, and P. Vaillant studied the effect of variations of *temperature* on the spectrum; G. Ciamician, J. F. Mohler, W. J. Humphreys, A. Kalähne, E. S. Ferry, J. Stark and M. Reich, M. Ritter, R. Küch and T. Retschinsky, etc., studied the effect of *pressure;* A. Kalähne, and E. S. Ferry, the effect of *current intensity;* J. Franck, the excitation potential of the mercury lines; G. M. J. McKay observed no evidence of emission lines from mercury at 3200° K; C. Füchtbauer, the excitation of the mercury lines by *ultra-violet rays;* H. P. Waran, the effect of a *magnetic field;* G. F. Hull, M. Ritter, and J. Stark and co-workers, the effect of an *electric field* on the spectral lines; P. Zeemann, A. A. Michelson, J. C. Shedd, H. M. Reese, H. Starke and J. Herweg, M. M. Risco, H. Nagaoka and T. Takamine, F. Paschen and co-workers, Lord Blythwood and E. W. Marchant, A. Gray and A. W. Stewart, C. Runge and F. Paschen, G. Berndt, E. Gehrcke and O. von Baeyer, H. Lunelund, W. Lohmann, T. Royds, W. Voigt, H. P. Waran, A. Landé, M. Tenani, H. Nagaoka, P. P. Koch, and P. Gmelin studied the **Zeemann-effect.** A. Landé, P. Lewis, P. G. Nutting, R. W. Wood, J. N. Collie, G. Berndt, E. Wiedemann, J. Stark, G. Gehlhoff, R. J. Strutt and A. Fowler, and H. Finger studied the influence of *impurities,* and C. Füchtbauer and G. Joos, the effect of nitrogen, hydrogen, and carbon dioxide on the spectrum of mercury. A. Hagenbach, A. Dufour, M. Glagoléeff, J. Stark and co-workers, G. F. Hull, etc., have studied the **Doppler effect.**

The **ultra-violet spectrum** of mercury was examined by L. and E. Bloch, W. Hallwachs, K. Wolff, F. Paschen, A. Tian, A. L. Hughes, J. M. Eder and E. Valenta, J. Courmont and C. Nogier, G. le Bon, E. Castelli, W. N. Hartley, G. D. Liveing and J. Dewar, F. Exner and E. Haschek, H. Lehmann and R. Straubel, J. Stark and S. Kinoshita, R. W. Wood and D. V. Guthrie, etc.; the **ultra-red spectrum,** by H. Lehmann, W. J. H. Moll, F. Paschen, W. W. Coblentz

and W. C. Geer, etc.; the **canal ray** spectrum, by J. Stark and co-workers, and G. F. Hull; the **cathode ray spectrum** by P. Lewis; and the spectrum from a glowing lime cathode in mercury vapour by F. Horton. J. J. Dobbie and J. J. Fox found the vapour of mercury shows very little absorptive power for light.

The **series spectrum** of mercury is more complex than those of zinc and cadmium. A comparison is shown in Fig. 3, Cap. 29. H. Kayser and C. Runge, and C. Runge and F. Paschen represent two series of triplets by the formulæ:

FIRST SERIES.	SECOND SERIES.
$\lambda^{-1}10^8 = 40159{\cdot}60 - 127484n^{-2} - 1252695n^{-4}$	$\lambda^{-1}10^8 = 40217{\cdot}98 - 126361n^{-2} - 613268n^{-4}$
$\lambda^{-1}10^8 = 44792{\cdot}87 - 127484n^{-2} - 1252695n^{-4}$	$\lambda^{-1}10^8 = 44851{\cdot}01 - 126361n^{-2} - 613268n^{-4}$
$\lambda^{-1}10^8 = 46560{\cdot}78 - 127484n^{-2} - 1252695n^{-4}$	$\lambda^{-1}10^8 = 46618{\cdot}44 - 126361n^{-2} - 613268n^{-4}$

These formulæ account for 25 out of over 95 lines in the arc spectrum, but some strong lines are not accounted for—*e.g.* 253·672. Other observations on the structure of the spectrum were made by J. R. Rydberg, C. Fabry and A. Perot, O. Lummer, R. J. Strutt, J. Barnes, L. Janicki, E. Gehrcke and O. von Baeyer, P. G. Nutting, B. Galitzin, F. Bates, H. Nagaoka, H. W. Webb, F. Paschen, H. Dingle, F. Paschen and E. Back, T. Royds, F. Horton, H. Hermann, S. R. Milner, H. Lunelund, G. Ciamician, W. N. Hartley, W. Ritz, A. Pflüger, L. Grebe, J. Franck and E. Einsporn, H. Stansfield, H. Konen, J. C. McLennan, J. Stark and co-workers, R. W. Wood, W. W. Coblentz, H. Gray, F. F. S. Bryson and J. Logie. R. Seeliger studied the conditions for the excitation of the different series of lines. G. Stead and B. S. Gossling found the **ionization potential** of mercury vap. to be 10·8 volts; J. C. McLennan and J. F. T. Young gave 10·45 volts. C. G. Found gave 10·1 volts; and A. L. Hughes and A. A. Dixon, 10·2 volts. K. T. Compton gave 4·65–4·99 volts for the minimum ionization potential. E. Einsporn and G. E. Gibson and W. A. Noyes have also measured this constant. J. F. Mohler and co-workers found 10·2 volts for the ionization potential, and 4·76–6·45 volts for the **resonance potential** of mercury vapour. M. N. Saha and E. Einsporn have made observations on this subject. J. A. Eldridge studied the energy losses in the ionization and resonance of mercury vapour; he also investigated the probability of collisions between electrons in mercury vapour. H. Sponer computed the frequency of the inelastic collisions of electrons producing the resonance line 2536·7 A. in mercury vapour. T. C. Hebb studied the effect of temp. on the **arcing voltage** of mercury; Y. T. Yao, K. T. Compton, and G. Stead and E. C. Stoner, the low voltage arc in mercury vapour; and G. Dejardin, the ionization of mercury in argon which begins at a potential of 11·3 volts; he also examined the effect with helium. The resulting spectra were also investigated.

The **electrical resistance** of mercury is the standard of reference for the International Ohm, which is defined as "the resistance offered to an unvarying electric current by a column of mercury at 0°, 14·4446 ± 0·00006 grms. in mass, of a constant cross-section, one sq. mm., and of a length of 106·245 ± 0·004 cms." Very many measurements have accordingly been made of the electrical resistance, or of the reciprocal, the **electrical conductivity,** of mercury—*e.g.* by A. Matthiessen and co-workers,[20] L. Lorenz, E. Becquerel, J. Müller, L. Grunmach, C. L. Weber, W. Siemens, L. Cailletet and E. Bouty, G. P. Grimaldi, Lord Rayleigh and H. Sidgwick, R. T. Glazebrook and T. C. Fitzpatrick, R. J. Strutt, H. Wuilleumier, L. Duncan, G. Wilkes and C. T. Hutchinson, J. V. Jones, W. Ortloff, A. Berget, H. Passavant, H. J. Rink, E. von Schweidler, A. Bernini, H. Schulze, etc. The sp. resistance of mercury at 18° is $0{\cdot}958 \times 10^{-4}$, and the relative increase per 1° is $+0{\cdot}92 \times 10^{-3}$. The reciprocal of the resistance of a cm. cube of mercury at 0° is nearly $1{\cdot}063 \times 10^4$ reciprocal ohms. E. Dorn gave $1{\cdot}06285 \times 10^4$. The electrical conductivity of liquid mercury in rec. ohms. $\times 10^{-4}$ between 0° and 350°, is:

0°	10°	25°	50°	100°	150°	200°	250°	300°	350°
1·063	1·0535	1·0386	1·0148	0·9685	0·9218	0·8751	0·8290	0·7831	0·7378

showing a steady decrease in the conductivity with rise of *temperature*. The values

of J. Dewar and J. A. Fleming, recalculated by H. Dickson, for solid mercury are ($\times 10^{-4}$):

−36·1°	−37·0°	−38·1°	−39·2°	−40·7°	−50·3°	−102·9°	−147·5°	−183·5°
1·24	1·44	2·205	2·74	3·46	4·70	6·65	9·46	14·35

showing a rapid increase in the conductivity as the temp. falls. The conductivity of solid mercury at the m.p. is 4·087 times as great as that of the liquid metal at the same temp. C. L. Weber found that the ratio of the resistance of the solid to that of the liquid at the f.p. is 0·27; L. Cailletet and E. Bouty, 0·24; G. Gehlhoff and F. Neumeier, 0·263; H. K. Onnes, 0·237; and L. Grunmach, 0·40. The high values are possibly explained by cracks in the frozen mercury. Mercury freezes in crystals which may have different conductivities in different directions, as is the case with bismuth and iron glance. The effect of temp. on the electrical conductivity is shown graphically in Fig. 6. H. K. Onnes found the resistance of mercury to fall to an extraordinary low value as the temp. approaches the b.p. of helium in vacuo, for if the resistance of liquid mercury at 0° be 172·7 ohms, or 39·7 ohms by extrapolation for the solid at 0°, it falls to 0·086 ohm at 4·3° K., and at 3° K. to 3×10^{-6} ohms—*i.e.* one millionth part of its value at 0° or 273° K. H. K. Onnes and J. Clay give for the resistance, R ohms, of mercury at very low temp.:

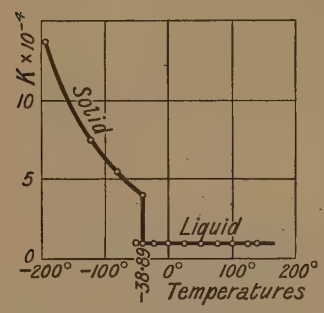

FIG. 6.—The Effect of Temperature on the Electrical Conductivity of Mercury.

	0°	−183·00°	−205·01°	−215·34°	−252·93⁵	−258·81°
R . .	97·126	7·2650	5·3900	4·5057	1·2613	0·7534

The resistance of the metals examined by H. K. Onnes becomes so extremely small as practically to vanish as the temp. approaches absolute zero. Thus supposing the resistance, R, of mercury at 0° or 273·1° K. is unity, then, at 20·1° K., R=0·05641; at 14·3° K., R=0·03369; at 4·3° K., R=0·0021; at 3·0° K., R=0·00003; and at 1·5° K., R=0·00000. Otherwise expressed, the resistance at 1·8° K., is barely one thousand millionth part of the value at ordinary temp., and at absolute zero, mercury will offer no measurable resistance to the passage of an electric current. H. K. Onnes calls this condition *super-conductivity*. A thread of mercury in that state will carry 1000 amps. without becoming warm, or setting up an e.m.f. at its ends. P. W. Bridgman found a discontinuity in the change of resistance with temp. just before the superconducting stage is reached; and he ascribed it to a polymorphic change of structure.

Several formulæ have been proposed to represent the relation between the temp. and the resistance of mercury. The temp. coeff. α for the resistance R at $\theta°$ in the formula $R=R_0(1+\alpha\theta)$, *i.e.* on the assumption that the resistance is proportional to the temp., is 0·0007443, according to A. Matthiessen and M. von Bose; 0·000889, E. W. von Siemens and J. G. Halske; 0·000869, Lord Rayleigh and H. Sidgwick; 0·000884, R. Lenz and N. Restzoff; 0·000895, E. Mascart, F. de Nerville, and R. Benoit; and 0·000907, K. Strecker. R. T. Glazebrook gave α=0·000879 between 0° and 15°; and K. Bornemann and G. von Rauschenplat give 0·000994 between 50° and 150°, and 0·000855 between 150° and 300°. There are, however, small deviations from the proportional law, for the temp. coeff. of the resistance increases as the temp. increases. D. Kreichgauer and W. Jäger gave $R=R_0(1+0{\cdot}0008827\theta+0{\cdot}000001260\theta^2)$ between 15° and 26°; C. Guillaume, $R=R_0(1+0{\cdot}000881\theta+0{\cdot}0000010100\theta^2)$ between 0° and 60°; R. Benoit, $R=R_0(1+0{\cdot}000882\theta+0{\cdot}000001140\theta^2)$ between 0° and 360°; G. Vicentini and D. Omodei, $R=R_0(1+0{\cdot}0008989\theta+0{\cdot}0_6 6695\theta^2+0{\cdot}0_8 10180\theta^3)$ between 0° and 350°; and F. E. Smith, $R=R_0(1+0{\cdot}00088788\theta+0{\cdot}0_5 10564\theta^2)$ in a Jena-glass tube and $R=R_0(1+0{\cdot}00088776\theta+0{\cdot}0_5 10376\theta^2)$ in a hard green-glass tube, between 0° and 22°. W. Jäger and H. von Steinwehr gave $R=R_0(1+889{\cdot}15$

$\times 10^{-6}\theta + 0{\cdot}99360 \times 10^{-6} \times \theta^2$) in a quartz vessel between 0° and 100°; and they also measured the conductivity of the isotopes of mercury. A. Baltruszajtis found the resistance of liquid mercury to be $R = R_0(1 + 0{\cdot}000882\theta + 0{\cdot}0_692\theta^2)$; and of solid mercury $R = R_m(1 + 0{\cdot}00456\theta)/(1 - 0{\cdot}00456 \times 38{\cdot}85)$ between the m.p. and −73°, where R_m denotes the resistance of the solid at the m.p. −38·85°. G. Wiedemann and R. Franz's ratio of the thermal conductivity, λ, and the electrical conductivity, κ, shows a small break at the m.p. as illustrated by the curve, Fig. 7. L. Lorenz's number, $\lambda/\kappa T$, is not proportional to the temp.

	−193°	−44°	−37°	−21°	0°	27°	100°	150°
$\lambda/\kappa \times 10^7$ . .	8·4	15·5	20·6	22·1	23·7	26·9	37·0	42·5
$\lambda/\kappa T \times 10^{10}$.	105	68	88	88	87	90	99	100

The effect of *pressure* on the resistance of mercury was found by R. Lenz to decrease about 0·02 per cent. per atm. A. Lafay found $dR/R = -0{\cdot}1251$ for 4500 kgrms. per sq. cm., *i.e.* about 0·02 per cent. per atm. C. Barus found a press. coeff. of −0·00003 up to 400 atm.; and A. de F. Palmer, −0·0000332 up to 2000 kgrms. per sq. cm. The last-named considers that the presence of occluded air is responsible for the high coeff. 0·0002 obtained by R. Lenz. According to C. Barus, therefore, $-dR/R = 30 \times 10^6 dp$; but, according to L. Grassi, $-dv/v = 3 \times 10^6 dp$; and by division, $dR/R = 10 dv/v$. Again, $dR/R = 800 \times 10^{-6} dT$; and $dv/v = 180 \times 10^{-6} dT$; and by division, $dR/R = 4{\cdot}4 dv/v$. P. W. Bridgman obtained the results indicated in Table VII for the effect of press. on the electrical resistance of mercury; and the results in Table VIII for the resistance of mercury at different press. and temp. when the resistance at atm. press. and the indicated temp. is unity. The resistances for the liquid were obtained by extrapolation beyond the f.p. It is estimated that the press. coeff. of the solid is between 0·000002 and 0·00002. The change in the resistance liquid-solid becomes less at higher press. and temp.; and the effect of press. on the resistance of the liquid is greater than it is on the solid. A. de F. Palmer and E. Lisell showed that the change in the electrical resistance of mercury by press. furnishes a means of measuring press., and the *mercury resistance gauge* was employed by P. W. Bridgman in his work on the effect of high press. on the properties of matter.

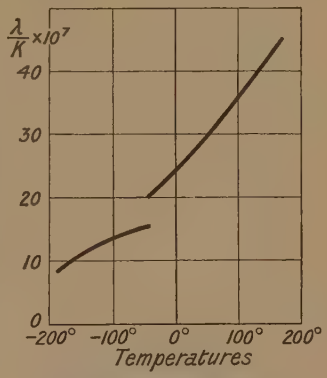

Fig. 7.—Effect of Temperature on G. Wiedemann and R. Franz's Ratio.

Table VII.—The Effect of Pressure on the Electrical Resistance of Mercury.

Press. kgrms. per sq. cm.	Resistance.						
	−75°	0°	25°	50°	75°	100°	125°
—	0·9186	1·0000	1·0240	1·0480	1·0719	1·0959	1·0970
500	0·9055	0·9689	0·9911	1·0137	1·0360	1·0574	1·0770
1000	0·8930	0·9400	0·9609	0·9823	1·0032	1·0224	1·0580
2000	0·8714	0·9136	0·9331	0·9533	0·9726	0·9902	1·0230
4000	0·8268	0·8804	0·9076	0·9268	0·9449	0·9611	0·9614
6000	0·7896	0·8667	0·8838	0·9023	0·9192	0·9345	0·9086
6500	0·7807	0·8459	0·8615	0·8793	0·8951	0·9096	0·8966
8000	—	0·8263	0·8408	0·8579	0·8729	0·8866	—
10000	—	—	0·8214	0·8377	0·8516	0·8650	—
12000	—	—	0·8034	0·8200	0·8318	0·8445	—

G. Berndt found that there is scarcely any change in the electrical resistance of mercury in a *magnetic field*; A. Hirschi, that the resistance of a column of mercury through which an *electric current* is flowing is greater than when no current is passing; and W. Jäger, that the resistance does not change when mercury is kept 6 years in a Jena-glass vessel—*vide supra*, F. E. Smith. W. Jäger and H. von Steinwehr measured the electrical conductivity of the different *isotopes* of mercury. If a thin triangular piece of amalgamated copper is floated on a trough of mercury, and a large direct current is passed through the bath, the piece moves across the bath blunt end foremost. E. F. Northrup explained the phenomenon as a result of the *pinch effect*, or the greater radial contraction of a conductor at the smaller than at the larger end; and C. Hering attributes the phenomenon to the tendency of the mercury conductor to stretch or lengthen itself more at one end than at the other owing to the greater density of the magnetic flux encircling the main path of the current being greater at the small end than at the larger end; and the effect is to make the lines of force act like compressed helical springs under unequal compression.

The effect of *impurities* in the mercury has also been investigated. Lord Rayleigh and H. Sidgwick found that the resistance of purified mercury is not affected by distillation in vacuo; and K. Strecker, that dissolved air does not change the resistance appreciably. R. Lenz and N. Restzoff could detect no

Table VIII.—The Change in Electrical Resistance when Mercury changes from Liquid to Solid at Different Pressures.

Temp. $\theta°$	Press. kgrms. per sq. cm.		Resistance in terms of that at atm. press. and $\theta°$.		
	Press. on solid.	Freezing press.	Solid.	Liquid.	Ratio.
16·2°	10960	10870	0·211	0·761	3·61
14·3°	10660	10490	0·247	0·764	3·09
10·0°	9960	9640	0·234	0·777	3·48
4·0°	9220	8450	0·251	0·791	3·15
0·0°	7660	7650	0·264	0·817	3·09
0·0°	7610	7650	0·241	0·816	3·39
−15·1°	5450	4680	0·258	0·863	3·35

difference in the conductivity of mercury in the presence and in the absence of mercuric oxide. W. Siemens found that additions of small quantities of metals —*e.g.* bismuth—which are bad conductors raise the conductivity of mercury. With the addition of a very small proportion of zinc, gold, or silver the conductivity is greater, and with the addition of a very small proportion of bismuth, lead, or tin greater than the value calculated from the volume of the mixture. A. Matthiessen has compared the observed conductivity with the result calculated from the relative vol. of mercury and the added metal. C. Michaelis stated that the conductivity of amalgams with up to 2·3 per cent. of zinc, cadmium, tin, lead, copper, silver, gold, and bismuth, is approximately the same as that calculated from the volume relations of the components. K. Bornemann and co-workers studied the effect of additions of the alkali metals.

The vapour of mercury was shown by W. Hittorf,[21] J. J. Thomson, and G. C. Schmidt, to be a very poor conductor of electricity. The electrical resistance of mercury vapour has been measured by H. Herwig, R. J. Strutt, P. C. Hewitt, A. P. Wills, etc. According to R. J. Strutt, the resistance of sat. mercury vapour at a red heat is much greater than that of the liquid, being 4×10^{-6} against 0·25. C. Wheatstone, in 1835, studied the brilliant light emitted when mercury is vaporized in an electric arc; and likewise also when zinc, cadmium, tin, bismuth, and lead are similarly treated. Patents for mercury lamps were obtained by E. H. Jackson,

1852; by C. Binks, about 1853; by J. T. Way, 1856; by C. W. Harrison, 1857; by C. W. Siemens, 1867; by W. Prosser, 1875; and by J. Rapieff, about 1879. H. J. Dowsing and H. S. Keating, 1896, made the first true mercury lamp in which a partially evacuated tube was employed, and P. Cooper-Hewitt's lamp appeared about 1901. Since clear fused quartz was introduced into commerce, various forms of mercury lamp with transparent fused quartz have been made—*e.g.* H. A. Kent and H. C. Lacell's lamp, and many others. In the modern *mercury arc lamp*, a long glass—or quartz glass—vessel is more or less exhausted. The vessel contains liquid mercury at one end, and this serves as cathode; a disc of iron or nickel serves as anode at the other end of the vessel. By tilting the body of the lamp so as to make a temporary short circuit between anode and cathode, by preheating the cathode surface with a spark discharge, or by some other device, mercury vaporizes, and a mercury arc is formed. The anode remains cold and non-luminous; the cathode also is non-luminous, so that the emission of light proceeds from the column of mercury vapour which carries the current. The anode is made with a large surface to prevent it becoming unduly heated, and such lamps can be operated only on direct current since the arc is extinguished when the current is reversed—*mercury interrupters*. If, however, the mercury vapour lamp has a glowing oxide electrode, the radiation of heat enables the mercury to volatilize, and the arc can be maintained with an alternating current. A. Sellerio studied the velocity of the arc stream between mercury and carbon.

W. R. Grove found that the metals can be arranged in a series according to their faculty of forming an electric arc—K, Na, Zn, Hg, Fe, Sn, Pb, Sb, Bi, Cu, Ag, Au, Pt. The mercury arc in a quartz glass vessel is an important source of ultra-violet light. J. Pollak estimated that 25 per cent. or more of the energy radiated by the lamp is lost for the production of light, and is wasted in the condensing chamber of the lamp. The properties of the mercury arc have been studied by J. H. Vincent, A. L. Hughes, A. Dufour, W. Hoepp, R. L. Morrison, S. R. Milner, P. A. Huguenin, K. von Natterer, F. M. Perkin, E. Darmois and M. Leblanc, C. Winther, G. Gehlhoff, E. Weintraub, M. Leblanc, M. von Recklinghausen, J. Rodet, J. Escard, R. Seeliger and G. Mierdel, etc. The electrodes have been discussed by R. de Valbreuze, L. Cassuto, H. E. Ives, O. Lehmann, J. Stark and co-workers, E. Urbain, C. Scal and A. Feige, etc. General reviews have been made by R. B. Hussey, M. Leblanc, etc.

Up to a certain current value of about 6·5 amps.—dependent on the geometrical shape of the lamp, and its external temp.—the arc voltage, E, decreases with increasing current, C, so that dE/dC is negative; at about 6·5 amps., dE/dC is zero, and if the current be increased beyond that value, dE/dC is positive, and the arc becomes stable. P. Küch and T. Retschinsky showed that the efficiency of the lamp expressed in Hefner's candles per watt, is relatively large and increases with the vap. press., and with the watt consumption—Fig. 8. The press. and temp. of the mercury arc lamp were studied by J. Stark and M. Reich, H. Buisson and C. Fabry, C. T. Knipp, L. Arons, etc. The potential gradient of the mercury arc lamp has been investigated by R. de Valbreuze, J. Pollak, A. Perot, J. Stark and co-workers, E. Warburg, A. P. Wills, P. C. Hewitt, etc.; and the luminescence and radiation of energy, by A. Perot and co-workers, C. Fabry and H. Buisson, H. Bordier, H. Rubens and O. von Baeyer, V. Henri, L. Grebe, C. D. Child, W. Matthies, H. Rubens and W. W. Coblentz, J. Pole, M. Boll, A. Tian, H. Busch, J. Stark, H. Herwig, and K. Burns. W. W. Coblentz and W. C. Geer's measurements of

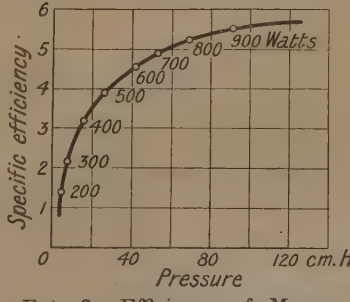

FIG. 8.—Efficiency of Mercury Vapour Lamp with Variations of the Pressure of the Mercury Vapour.

the distribution of energy are illustrated by the diagram, Fig. 9. The visible radiation is confined principally to two sharp lines, Hg_α with $\lambda=0{\cdot}546\mu$, and Hg_β with $\lambda=0{\cdot}579\mu$. The light from the mercury arc is accordingly of a livid bluish-green colour, and it lacks the warmer and richer hues of ordinary light. This subject has been discussed by J. H. Gladstone, H. E. Ives, A. J. Marshall, etc. A. Günther-Schulze studied the cathode phenomena in the electric arc; G. E. Gibson and W. A. Noyes, the **luminous discharge** in mercury vapour; and A. Hörnli, the ultra-violet light from the mercury arc.

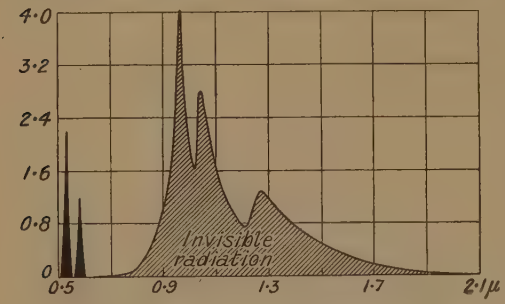

Fig. 9.—Spectrum of the Energy Radiation from the Mercury Arc.

J. W. Ritter [22] placed mercury near the middle of the **electro-chemical series**, and G. Wiedemann believed that mercury is more readily charged with positive than with negative electricity. According to W. Hankel, if the potential difference—the **Volta effect**—between zinc and copper is 100, that of mercury with aluminium is 101 to 106; with zinc, 81; with cadmium, 62; with lead, 37; with tin, 30; with antimony, 12; with bismuth, 11; with nickel-brass, 6; with brass, 3; with iron, −3 to −11; with copper, −19; with gold, −29; with palladium, −34; with silver, −37; with coke, −41; and with platinum, −42. W. E. Ayrton and J. Perry, O. J. Lodge, C. Hockin and H. A. Taylor, and R. B. Clifton measured the contact potential of mercury and copper; R. B. Clifton, against iron; and R. B. Clifton, and C. Hockin and H. A. Taylor, against zinc. H. Pellet found that against soft gold, the contact potential is −0·06 volt, and against hard gold, +0·04 volt. F. Exner and J. Tuma found the contact potential against sodium is 2·47; magnesium, 1·38; zinc, 1·08; aluminium, 0·98; lead, 0·72; tin, 0·67; iron, 0·56; copper, 0·33; silver, 0·18; platinum, 0·05; gold, 0·05; and carbon zero. A. Gouy found that the contact potential of mercury with its amalgams is zero, and with other metals very small. E. Obach obtained no current between mercury and zinc, cadmium, tin, platinum, or iron. C. Christiansen measured the potential difference of mercury against magnesium, aluminium, zinc, tin, lead, iron, copper, or carbon at 20° in the presence of air, hydrogen, oxygen, or carbon dioxide. E. Perucca measured the Volta effect in the Zn-Hg, Cd-Hg, Bi-Hg, and Sb-Hg couples in vacuo and in various gases; and with the Hg-Pt couple in air, nitrogen, carbon dioxide, and hydrogen.

J. Canton found that mercury is negatively charged when a piece of glass, shellac, amber, or calcspar is dipped into the liquid; according to J. P. Dessaignes, the results with shellac, silk, wool or glass, and mercury differ according to the degree of purity of the element. L. Hart found that mercury is negatively charged by friction on the walls of a capillary, and when it is broken up into beads by an air-blast. J. Dechant noted that mercury is electrically charged when filtered through leather, and this the more the finer the pores. A. Gaugain studied the charging of mercury with electricity by friction with other metals. E. Perucca found that a freshly made surface of mercury is strongly electrified positively if placed in contact with glass, paraffin, sealing-wax, ebonite, wool, etc., but after a time, the surface of mercury loses its positive charge, passes through a neutral stage, and then acquires a negative charge which gradually increases to a limiting value. A. Coehn and A. Lotz also found that mercury in vacuo is positively electrified with respect to glass. J. Heyrovsky studied the electrolysis of soln. of alkali or alkaline earth salts with mercury drops as electrode.

C. Matteucci [23] could detect no **thermoelectric force** between hot and cold mercury. The subject was further investigated by G. Gore, G. Magnus, F. C. Henrici,

V. de Heer, T. des Coudres, and A. Peltier. The thermoelectric force of mercury against liquid and solid amalgams was studied by A. Battelli. A. Seebeck, W. Hankel, P. Bachmetjeff, and J. Cumming have investigated the position of mercury in the thermoelectric series. Warm mercury and the cold metal give a current from hot to cold with bismuth, platinum, copper, silver, lead, tin, zinc, mercury, and gold; and from cold to hot with antimony, arsenic, and iron. The effect of press. has been studied by E. Wagner, E. Siegel, T. des Coudres, H. Agricola, A. H. Bucherer, and H. Hörig. The Thomson effect has been studied by W. Thomson, F. Braun, J. Königsberger and J. Weiss, H. Haga, P. Cermak, C. Schoute, and T. des Coudres. F. Braun found the thermoelectric force with the *lead-mercury* couple to be −3·93 microvolts at 50°; K. Noll gave −4·03. A. Matthiessen gave 2·52 for the *silver-mercury* couple between 4° and 48°, when that of the silver-copper couple is unity. E. Becquerel gave −0·000483 volt for the *copper-mercury* couple, and A. Gaugain found the e.m.f. rises more rapidly than the temp. G. Gehlhoff and F. Neumeier's value for the thermoelectric force of copper-mercury couple, $dE/d\theta$, is:

	−193°	−78·4°	−37·6°	0°	50·5°	99·9°	149·4°
$dE/d\theta$ . .	0	2·02	5·59	6·11	7·55	9·32	10·91μ volts.

with a marked break at the m.p. E. Oosterhius studied the iron-mercury couple, and found at 16·2° the e.m.f. is 2692×10^{-7} volts at 98°, 15935×10^{-7} volt; and at 182·6°, 28280×10^{-7} volt; and the Peltier effect is $1·1644\times10^{-3}$ grm. cal. at 18·45°; $1·388\times10^{-3}$ grm. cal. at 99·64; and $1·511\times10^{-3}$ grm. cal. at 182·3°. P. Cermak's values for the Thomson effect $\times10^7$ in cals. are −4·20 at 47°; −5·11 at 71°; −5·88 at 179°; and −4·98 at 262°. K. Noll found at 100° the *mercury-platinum* couple gives 0 millivolt; E. Becquerel gave −0·07 and E. Wagner 0·04 millivolt. A. Battelli found for *zinc-mercury* and *brass-mercury* couples respectively −71·620 and −50·126 microvolts at 20°, rising to −1429·000 and −820·940 microvolts at 200° respectively. K. Noll found for a temp. difference of 100°, in microvolts, bismuth, −6705·4; ordinary *nickel*, −1643·3; purified *nickel*, −1448·37; *cobalt*, −1522·2; *nickel-brass*, −1079·9; *tin*, 391·44; *lead*, 402·5; *brass*, 439·38; *silver*, 690·88; *gold*, 713·35; *copper*, 726·62; *zinc*, 713·96; *cadmium*, 867·41; *iron*, 1592·2; *antimony*, 3379·6; and *carbon*, 1452. W. Peddie and A. B. Shand found the thermoelectric current of solid mercury gives a curve nearly continuous with that of liquid mercury. P. Cermak measured the thermoelectric force and the Peltier effect of mercury against constantin. G. Gore, and C. R. A. Wright and C. Thompson measured the thermoelectric force of mercury against a number of *salt solutions*.

S. Marianini[24] placed mercury at the negative end of the series with respect to the difference of potential in sea-water acidified with $\frac{1}{100}N$-sulphuric acid; A. de la Rive put mercury between tin and lead, and H. C. Oersted between arsenic and silver, with respect to dil. sulphuric acid. A. de la Rive put mercury between lead and silver with respect to conc. nitric acid; J. C. Poggendorff between silver and cupric sulphide with respect to a soln. of ammonium chloride; and between lead and palladium with respect to a soln. of potassium cyanide. W. Ostwald found mercury to be electronegative with respect to acids; and J. Brown, with respect to electrolytes generally. A. von Antropoff found that in hydrogen peroxide, mercury becomes more electropositive in the presence of alkalies, and more electronegative in the presence of acids.

H. Pellat found the potential difference of mercury towards mercurous nitrate is zero, but it may be considerable in the presence of other electrolytes. C. Hockin and H. H. Taylor found that when mercury is alloyed with one or more metals, it becomes very much more electropositive towards dil. sulphuric acid, and soln. of zinc sulphate; S. Lindeck, indeed, found that 0·0005 per cent. of foreign metal had an appreciable action, and this the more the more positive the added metal. W. C. Sabine and G. Lippmann found that when purified and impure mercury are

immersed in vessels in water, and in electrical contact, a current flows through the water to the impure mercury. If two mercury electrodes in electrical contact are dipped at different times in a conducting but indifferent liquid—water, alcohol, glycerol, salt-soln., hydrochloric acid, etc.—G. Quincke found that a current is produced.

N. T. M. Wilsmore estimated the **electrolytic potential** of mercury against a normal ionized soln. to be —0·750 volt; W. Ostwald gave —0·99 volt; and B. Neumann gave against a sat. soln. of *mercurous sulphate*, —0·980 volt. Other measurements have been made by W. E. Ayrton and J. Perry, V. Rothmund, E. Rothé, C. R. A. Wright and C. Thompson, F. Auerbach, L. Sauer, etc. B. Neumann found the potential of mercury against a soln. of *mercurous nitrate* to be —1·028 volt, or —1·027 volt, according to N. T. M. Wilsmore. Other measurements have been made by F. Fischer, R. Behrend, H. Pellat, C. R. A. Wright and C. Thompson. For *mercurous chloride*, the normal calomel electrode, W. Ostwald and W. C. McC. Lewis gave 0·61; and L. Sauer found for Hg | *N*-KCl, HgCl-electrode, 0·560 volt at 18°. W. Palmaer, N. T. M. Wilsmore, C. R. A. Wright and C. Thompson, H. A. Fales and W. A. Mudge, F. H. Getman, H. Freundlich and E. Mäkelt, J. Billitzer, R. Luther, E. Rothé, E. Amelung, N. E. Loomis, and S. F. Acree, F. Auerbach, etc., have measured the potential of the calomel electrode. The temp. coeff. has been measured by L. Sauer, G. W. Coggeshall, and T. W. Richards. F. Auerbach, R. Luther and F. Pokorny, F. G. Donnan and A. J. Allmand, etc., measured the potential of the electrodes Hg | HgO, KOHaq., and of Hg | HgO, KOHaq. R. Luther found that the potential of a soln. of a mercurous salt and mercury is about 223 times that of a soln. of a mercuric salt of the same dilution. F. M. G. Johnson and N. T. M. Wilsmore found the potential of mercury against *water* to be —0·329 volt, and W. Hankel found that if the contact potential of Zn-Cu be 100, that of mercury against water is at first —6, falling after some time to —30; other measurements were made by F. Exner.

R. Blondlot and E. Bichat found for *sulphuric acid*, 0·842 volt; H. Pellat, F. Paschen, and A. König also measured the potential of mercury against sulphuric acid. F. Exner measured the potential of mercury against *chlorine water*, *bromine water*, and *iodine water*; F. Exner, and F. Paschen against *hydrofluoric acid*; F. Paschen, F. Exner, and A. König, against *hydrochloric acid*; F. Exner and V. Rothmund, against *hydrobromic acid*; F. Exner, against *hydriodic acid*; F. Paschen, and R. Behrend, against *potassium hydroxide*; A. König, F. Paschen, and R. Behrend, against *sodium hydroxide*; C. Immerwahr, against *barium hydroxide*; F. Paschen, C. Immerwahr, and R. Behrend, against *potassium chloride*; R. Behrend, against *potassium bromide*; F. Paschen, R. Behrend, V. Rothmund, and H. Brandenburg, against *potassium iodide*; R. Behrend, against *complex iodides*; C. R. A. Wright and C. Thompson, against the *silver halides* suspended in soln. of the corresponding halide; and *zinc chloride*, *cadmium chloride*, and *mercurous bromide and iodide* suspended in soln. of the corresponding zinc halide; F. M. G. Johnson and N. T. M. Wilsmore, of a soln. of mercuric iodide in *liquid ammonia*. A. König, and F. Paschen, against *nitric acid*; G. Gore, against *ammonium, potassium, and sodium nitrates*; C. R. A. Wright and C. Thompson, against *silver nitrate*; G. Gore, against *strontium* and *barium nitrates*; S. Labendzinsky, against *zinc nitrate, cadmium nitrate, lead nitrate, cobalt nitrate* and *nickel nitrate*. F. Paschen, and G. Gore, against *potassium sulphate*; A. König, and G. Gore, against *sodium sulphate*; G. Gore against *ammonium sulphate, ammonium aluminium sulphate, sodium selenate*; and *sodium sulphite*; A. König, against *magnesium sulphate*; A. König, and S. Lindeck, against *zinc sulphate*; G. A. Hulett and R. E. de Lury, against *cadmium sulphate*; F. Paschen, against *ferrous sulphate*. F. Paschen, R. Behrend, and G. Gore, against *sodium carbonate*; F. Paschen, C. Immerwahr, and G. Gore, against *potassium carbonate*; F. Paschen, C. Immerwahr, S. B. Christy, and V. Rothmund and G. Gore, against *potassium cyanide*; F. Paschen, and R. Behrend, against *mercuric cyanide*; C. Immerwahr, R. Behrend, and V. Rothmund, against *potassium thiocyanate*. C. Immerwahr, and R. Behrend measured the potential of mercury against soln. of *potassium dichromate*; C. Immerwahr, and R. Behrend, against *sodium hydrophosphate*; C. Immerwahr, against *ammonia complexes*; R. Behrend, against *ammonium chloride*; R. Behrend, against *ammonium hydroxide*; C. Immerwahr, against *hydrogen sulphide*; C. Immerwahr, R. Behrend, and V. Rothmund, against *sodium sulphide*; H. Brandenburg against *potassium sulphide*; R. Behrend, against *potassium tartrate*; R. Behrend, against *potassium oxalate*; G. Gore, against *formic acid* and *sodium formate*; R. Behrend, against *urea*; R. Behrend,

H. Brandenburg, and G. Gore, against *sodium thiosulphate* ; G. Gore, against *sodium*, and *ammonium phosphates* ; *sodium diborate* ; and *boric acid*.

K. Bornemann [25] measured the e.m.f. of the cell Hg | H_2O_2 | Hg. E. Neumann studied the cell with Hg and H_2SO_4 against Hg and a sat. soln. of mercurous sulphate, and found it to be remarkably constant. E. C. Sullivan studied the cell with Hg | HgCl, and hydrochloric acid against Hg | HgCl and a soln. of potassium chloride ; and A. Lapworth and J. R. Partington against Hg | HgCl and hydrochloric acid (concentration cell) ; V. Rothmund studied the cell with Hg | HgCl, and a soln. of potassium chloride against mercury and a sulphuric acid soln. of mercurous sulphate ; S. Bugarszky against mercury and a soln. of mercurous bromide in potassium bromide, of mercurous iodide in potassium iodide, of mercuric sulphide in potassium hydrosulphide ; of mercurous nitrate in potassium nitrate, of mercurous oxide in potassium hydroxide, and of mercurous sulphate in potassium sulphate ; and R. Luther and F. Pokorny against mercury and a soln. of mercurous sulphate in potassium sulphate. J. von Hepperberger studied conc. cells of zinc sulphate soln. with mercury electrodes ; E. Biron, conc. cells of cadmium chloride with calomel electrodes ; and R. Abegg, and M. S. Sherill, conc. cells of mercuric bromide, and iodide, and mercuric cyanide with mercury electrodes ; A. Ogg studied cells with mercury and a nitric acid soln. of mercurous nitrate against mercury with a nitric acid soln. of silver nitrate : S. Bugarszky, cells with mercury and a soln. of mercurous bromide in potassium bromide, of mercurous iodide in potassium iodide, or of mercurous oxide in potassium hydroxide, against mercury and a potassium acetate soln. of mercurous acetate. S. W. J. Smith and H. Moss studied the e.m.f. of soln. with electrodes of mercury at rest and in motion. F. Paschen found that a mercury anode polarizes more quickly in hydrochloric acid than in sulphuric acid, and he attributed this to the formation of a coherent film of calomel ; A. W. Laubengayer also showed that the apparent irreversibility of the calomel electrode is due to the formation of a strongly adsorbed film of mercurous chloride on the surface of the mercury anode ; this film offers a high resistance to the passage of the current.

The electromotive force of various cells with mercury as one electrode and another metal as cathode, and different acids, bases, and salt soln. as electrolytes, has been studied by A. Oberbeck and J. Edler.[26] F. Streintz measured the e.m.f. of mercury and sulphuric acid against silver and silver sulphate ; copper and copper sulphate ; bismuth and bismuth sulphate ; cobalt and cobalt sulphate ; tin and stannous sulphate ; cadmium and cadmium sulphate ; zinc and zinc sulphate ; and against magnesium and magnesium sulphate. M. H. Jacobi measured the e.m.f. of mercury and nitric acid against a soln. of potassium cyanide and zinc, copper, cadmium, tin, silver, nickel, antimony, lead, and mercury. The cell with mercury and a soln. of mercuric oxide in one of sodium hydroxide against the hydrogen electrode has been investigated by J. N. Brönsted, and R. Luther and F. Pokorny ; the cell with mercury and a soln. of mercurous sulphate in sulphuric acid against the hydrogen electrode by R. Luther and F. Pokorny, and A. C. Chapman and H. D. Law ; mercury and a soln. of mercuric sulphate against copper or copper amalgam and cupric sulphate by L. W. Oeholm ; mercury and a soln. of zinc sulphate against zinc by J. Moser, J. M. Gaugain, and C. Hockin and H. A. Taylor ; mercury and a soln. of cadmium sulphate against cadmium by C. Hockin and H. A. Taylor ; mercury and mercuric chloride against zinc chloride and zinc by H. von Helmholtz, and V. Buscemi ; mercury and mercurous chloride against zinc and zinc chloride, cadmium and cadmium chloride, copper and cupric chloride, or iron and ferrous chloride by S. Czapsky, T. Godlewsky, and F. Streintz ; mercury, mercurous chloride, and zinc chloride against lead chloride and lead by P. Chroustchoff and A. Sitnikoff ; mercury and a carbonic acid soln. of mercuric carbonate against zinc by G. A. Hulett ; mercury and cupric sulphate against copper by J. Moser, N. A. Puschin, C. L. Speyers, and J. C. Poggendorff ; mercury and a sat. soln. of zinc sulphate in sulphuric acid against zinc and zinc sulphate by

W. Kistiakowsky ; mercury and a soln. of mercurous chloride in potassium chloride against zinc and zinc sulphate by W. Kistiakowsky ; against cadmium and cadmium chloride by E. Biron ; against silver, silver chloride, and cadmium chloride by E. Biron ; against silver chloride and silver by P. Chroustchoff and A. Sitnikoff ; and against hydrochloric acid and platinum by N. E. Loomis and S. F. Acree ; mercury and mercurous chloride against lead and lead chloride by F. Pollitzer, E. Cohen, and R. Luther ; and against silver chloride and silver by F. Pollitzer, and J. N. Brönsted. J. Regnauld measured the e.m.f. of mercury and of soln. of potassium iodide with chlorine, bromine, or iodine against carbon and a soln. of potassium iodide. M. le Blanc measured the e.m.f. of the cells with mercury and a normal soln. of the chlorides of sodium, potassium, lithium, magnesium, calcium, strontium, barium, and zinc against an amalgam with the corresponding metal. C. Hockin and H. A. Taylor studied the e.m.f. of many amalgams and alloys against mercury and sulphuric acid ; F. Paschen, the e.m.f. of mercury and a soln. of zinc sulphate against zinc amalgam ; and C. L. Speyer, the e.m.f. of the same cell with soln. of various salts and acids.

F. M. G. Johnson and N. T. M. Wilsmore [27] studied cells with soln. of liquid ammonia ; L. Kahlenberg, in pyridine ; and J. Neustadt and R. Abegg, in methyl alcohol, and ethyl alcohol ; W. Negbauer studied cells with fused salts ; and G. Meyer, cells with glass as the electrolyte.

The unit of electrical press., the volt, is defined by the Board of Trade as that which if steadily applied to a conductor whose resistance is one ohm, will produce a current of one ampère, and is represented by 0·6974(1000/1434) of the electrical press., at a temp. of 15°, between the poles of the standard voltaic cell known as Clark's and set up in a specified way. The e.m.f. of a standard cell should be readily reproduced ; it should not change with age ; and the changes should vary in a definite way when the temp. changes. The silver chloride cell of W. de la Rue [28] was used at one time as a standard cell, but it proved to be unsatisfactory. F. M. Raoult, O. J. Lodge, and J. A. Fleming attempted to use a form of Daniell's cell as a standard, but it was proved to be troublesome. Forms of the cell proposed in 1873 by L. Clark have proved to be the most successful standard cell.

Four standard cells with a mercury electrode have attracted some attention, A. Gouy's, H. von Helmholtz's, E. Weston's, and L. Clark's. The general characters of standard cells have been discussed by W. Jäger,[29] G. A. Hulett, K. Kahle, J. Klemencic, C. J. J. Fox, P. J. H. van Ginneken, T. Wulf, etc. The thermodynamics of standard cells have been studied by E. J. Cohen and co-workers, R. A. Lehfeld, H. Rupp, L. G. Gouy, W. Jäger, H. von Helmholtz, D. McIntosh, G. A. Hulett.

In **Clark's standard cell,**[30] Zn | $ZnSO_4$ | Hg_2SO_4 | Hg, the reaction $Zn+HgSO_4 \rightleftharpoons ZnSO_4+2Hg$, goes from left to right during the discharge, and F. Pollitzer gives 82,402 cals. for the thermal value of this reaction at 18°. The preparation of cells of different form has been described by R. T. Glazebrook and S. Skinner, A. E. Köhler, H. L. Callendar and H. T. Barnes, H. S. Carhart, K. Feussner, Lord Rayleigh, W. Jäger, K. Kahle, J. Swinburne, W. R. Cooper, etc. E. Cohen and P. J. H. van Ginneken have shown that the cell gives good results between 20° and 38°. The e.m.f. at 15° was found to be 1·4378 volts by L. Clark ; 1·4329 volts by H. S. Carhart ; 1·4345 volts by Lord Rayleigh ; 1·4344 volts by R. T. Glazebrook and S. Skinner ; 1·4322 volts by K. Kahle ; 1·4328 volts by W. Jäger and K. Kahle ; 1·4333 volts by H. S. Carhart and K. E. Guthe ; 1·434 volts by A. von Ettinghausen ; and 1·4323 volts by W. E. Ayrton, T. Mather, and F. E. Smith. G. A. Hulett found 1·4240 volts at 25° and 1·43300 volts at 15°. The e.m.f. has been studied by many others—H. T. Barnes, F. Pollitzer, W. Kistiakowsky, S. Lindeck, F. S. Spiers, B. S. Twyman, and W. L. Walters, A. P. Trotter, E. J. Cohen, etc. W. Jäger and K. Kahle gave for the effect of temp. at $\theta°$ between 0° and 30° $E = 1·4328 - 0·00119(\theta - 15) - 0·000007(\theta - 15)^2$ volt ; H. L. Callendar and H. T. Barnes gave $E = E_{15°} - 0·001200(\theta - 15) - 0·0000062(\theta - 15)^2$; and Lord

Rayleigh gave $E=E_{15°}\{1-0{\cdot}00077(\theta-15)\}$. E. Cohen and L. R. Sinnige studied the effect of press.

The relatively large temp. coeff. of Clark's cell is due to the large variation in the solubility of zinc sulphate with variations of temp., and in order to reduce the temp. coeff., E. Weston [31] recommended cadmium sulphate because the solubility changes relatively little with temp. He also used an alloy of cadmium in place of zinc; and he thus reduced the temp. coeff. to 0·01 per cent. The combination in **Weston's standard cell** is therefore Cd | $CdSO_4$ | Hg_2SO_4 | Hg, and the reaction is $Cd+Hg_2SO_4 \rightleftharpoons CdSO_4+2Hg$, from left to right when the cell is discharging. The effect of using cadmium amalgam has been studied by E. Cohen, J. Obata, F. E. Smith, S. W. J. Smith, C. H. Wind, H. C. Bijl, G. A. Hulett, etc. The construction of the cell has been discussed by W. Jäger and co-workers, E. Cohen and co-workers, G. A. Hulett and co-workers, H. T. Barnes, C. H. Wind, P. J. H. van Ginneken, F. E. Smith, J. Henderson, A. Dearlove, E. Cohen and T. Kohnstamm, J. Blondin, H. C. Bijl, etc. The effect of different cadmium amalgams on the e.m.f. of the cell has been treated by W. Reinders, F. E. Smith, H. C. Bijl, W. Jäger and S. Lindeck, E. Cohen and co-workers, etc. According to J. Boerema, the e.m.f. of the cell at 17° is 1·01833 volts; E. Warburg gave 1·0183 volts at 20°; P. Janet and co-workers, 1·01836 volts at 20°; W. E. Ayrton and co-workers, 1·018305 volts at 17°; W. Jäger, 1·0190 volts; E. Cohen, 1·0185 volts at 25°; G. A. Hulett, 1·01843 volts at 25°; and R. de Baillehache, 1·01836 volts at 17°. Other observations have been made by F. E. Smith, S. N. Taylor, W. Jäger and co-workers, W. Marek, etc. A. N. Shaw and H. E. Reilley studied the ageing of the Weston cell. S. W. J. Smith found the temp. coeff. of the cell at 5° to be zero, above 5° it is positive, and below, negative. F. A. Wolff gave for the e.m.f. of the cell at $\theta°$, $E=1{\cdot}0184-0{\cdot}00004075(\theta-20)-0{\cdot}0_6944(\theta-20)^2+0{\cdot}0_898(\theta-20)^3$; F. E. Smith, $E=E_{17°}-0{\cdot}0000345(\theta-17)-0{\cdot}0_666(\theta-17)^2$; W. Jäger, $E=1{\cdot}0186-0{\cdot}0_438(\theta-20)-0{\cdot}0_665(\theta-20)^2$. Other observations have been made by W. Jäger and co-workers, H. von Steinwehr, H. T. Barnes, P. Janet and R. Jouast, H. C. Bijl, A. Dearlove, S. Czapsky, E. Cohen and H. R. Kruyt, etc.

Attempts [32] have been made to prepare standard cells of exactly one volt, but the practical advantage does not amount to much. In **Helmholtz's standard cell,** Zn | $ZnCl_2$ | HgCl | Hg, the e.m.f. is nearly one volt when the sp. gr. of the soln. of zinc chloride is 1·391 at 15°. An increase of 16 per cent. in the sp. gr. of the soln. diminished the e.m.f. by 3·5 per cent. Cells of this type, with unsaturated soln., should be sealed so that evaporation may not change the sp. gr. of the soln. H. S. Carhart gave for the e.m.f. at $\theta°$, $E=1+0{\cdot}000094(\theta-15)$, showing that the temp. coeff. is positive. According to W. Hibbert, the temp. coeff. is 0·000085 volt per degree. The cell has also been studied by W. Ostwald, and W. Jäger. **Gouy's standard cell,**[33] Zn | $ZnSO_4$ | HgO | Hg, is not reversible. The e.m.f. is about 1·4 volts, with a negative temp. coeff. of about 0·0002 volt per degree. S. Lindeck, R. T. Glazebrook and S. Skinner, W. Jäger, C. Limb have studied the cell. According to W. Jäger, the cell Cd | $CdCl_2$ | HgCl | Hg, with an e.m.f. of about 0·75 volt, and a negative temp. coeff. of 0·00025 volt per degree, is not suitable as a standard cell. J. Obata studied the e.m.f. of the standard cell Hg | Hg_2SO_4, $CuSO_4$ | $Cu_{amalgam}$.

W. Ostwald [34] gave −20 Cals. for the **heat of ionization** of the $Hg^{··}$-ion from the element, and W. R. Bousfield and T. M. Lowry −19·28 Cals. for the $Hg^{·}$-ion, while that of hydrogen is −0·6 Cal. W. Ostwald also gave −20500 cals. per valence. J. Stark, A. S. Eve, P. Drude, R. Pohl, R. Fürstenau, R. Schenk, etc., have studied the relation between the electrons and molecule of mercury. The **transport numbers** of ions have been measured by E. Rieger, J. F. Daniell and W. A. Miller, W. Hittorf, A. Chassy, C. L. Weber, J. Moser, G. Kümmell, R. Gans, P. Straneo, and S. Lussana. The **electrochemical equivalent** of mercury has been measured by R. Abegg, H. Buff, etc.; 3·7352 grms. of mercury separate per ampère-hour from soln. of mercuric salts.

The **decomposition voltages** of many mercury salts have been measured by

R. Abegg and G. Bodländer, A. Coehn and E. Neumann, E. Abel, E. Bose, J. E. Root, F. Glaser, W. Kettembeil, W. D. Bancroft, etc.[35] The electrolytic **solution pressure** is given as $3{\cdot}1\times10^{-16}$ atm. by B. Neumann; and the soln. press., that is, the excess press. against the press. of the ions, calculated by W. Ostwald from the observations of F. Braun and C. R. A. Wright and C. Thompson, is approximately 10^{-15} atm. The **overvoltage of hydrogen** on a mercury electrode is about 0·8 volt. corresponding with bivalent mercury; 0·4 volt corresponding with univalent mercury; and zero voltage corresponding with non-valent mercury. According to E. Newbery:

> The first state is produced by, and is permanent at, low-current densities, and is generally shown by fresh mercury. The second state is shown by mercury which has been kept for some time in contact with dil. acid, and appears to be unstable when a current is flowing. It may be due to the formation of traces of mercurous salt absorbed on the mercury surface and also carried into the body of the mercury by movements due to change of surface tension. This salt on decomposing would tend to give the hydride corresponding with univalent mercury, and therefore the lower overvoltage. The third state is permanent at high-current densities, and when once acquired takes a considerable time for its removal. Its sudden appearance is accompanied by an equally sudden change in the size of the bubbles of gas liberated, from large to very small.

The overvoltage of mercury has been measured by W. A. Caspari,[36] A. Coehn, J. Tafel, E. Müller, S. Dunnill, E. Newbery, H. G. Möller, J. W. Walker and C. S. Paterson, and G. N. Lewis and R. F. Jackson. G. Carrara found 0·77 volt in methyl alcohol soln., and 0·56 volt in ethyl alcohol soln. The **polarization** of the mercury cathode has been studied by E. Warburg,[37] W. Lietzau, E. Rothé, J. Roschkowsky, M. le Blanc, G. Lippmann, E. Bouty, F. Streintz, J. Tafel, F. Teltscher, G. N. Lewis and R. F. Jackson, etc. S. Dunnill studied the overvoltage of the mercury cathode. S. Magrini observed a curious effect of electrolytic polarization and depolarization with the consequent variations in the surface tension and form of a drop of mercury:

> When the end of a piece of clean magnesium wire is brought just into contact with a drop of mercury placed in a basin or watch-glass and covered with 0·1—0·2 per cent. hydrochloric acid, the mercury at once begins to undergo rhythmic contraction and distensions, the movements continuing until the magnesium wire is removed. If the end of the wire is central to the upper part of the drop, the rhythmic movement produces a surface undulated in concentric rings, whereas if a non-central position is occupied by the wire, an undulating ellipsoidal form results, this undergoing rhythmic contraction and distension in directions mostly perpendicular to one another. The rapidity of the oscillations varies with the magnitude of the drop. The same phenomenon is observed if the hydrochloric acid is replaced by a soln. of potassium hydroxide, sodium carbonate, ammonia, etc., but it seems necessary that hydrogen should be evolved by either direct or secondary chemical action. The phenomenon is especially marked with an aluminium wire and a soln. of potassium cyanide. With an iron wire and hydrochloric acid soln., the movement of the mercury occurs only if the wire is applied to the side of the mercury where the curvature of the drop is greater than at the upper surface.

E. Perucca studied the **electrification** of mercury by friction; M. König, the electrostatic charge carried by fine particles of mercury falling in different gases; H. Schüler, the cathode and anode drop in mercury vacuum arc; H. Sponer, the effect of **colliding electrons** on the mercury atom; and J. S. van der Lingen, J. K. Robertson, and J. von Kowalsky, the **electrodeless discharge** in mercury vapour. E. Bouty measured the **dielectric cohesion** of mercury vapour. Y. T. Yao studied the low voltage arc in mercury vapour.

According to M. Faraday,[38] mercury is diamagnetic. G. Quincke found the **magnetic susceptibility** to be, air unity, $-2{\cdot}6\times10^{-6}$ vol. units at 19°; S. Meyer found $-2{\cdot}1\times10^{-6}$ vol. units at 15°; K. Honda, $-0{\cdot}193\times10^{-6}$ mass units at 18°; and G. Meslin, $0{\cdot}19\times10^{-6}$ mass units; K. Honda said that the magnetic susceptibility remained constant between atm. temp. and the b.p., but M. Owen found it to increase numerically in passing from —170° to —39°. A. Dufour found a magnetic field lengthened the stream of mercury flowing from a capillary tube.

C. Maurain used mercury as an electromagnetic screen. G. Berndt found that

a magnetic field scarcely affected the electrical resistance of mercury; and T. des Coudres likewise observed no change in the thermoelectric properties in the magnetic field. A. Dufour studied the rotation of the arc in a magnetic field, and A. Perot, the effect of a magnetic field on the luminosity of the arc light in a vacuum tube. P. Pascal measured the magnetic sensitiveness; W. N. Fenninger, the **Hall effect**; and H. Geipel, the magnetic properties at the temp. of liquid air.

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§ 4. The Chemical Properties of Mercury

Mercury is not altered by shaking it in an atm. of **hydrogen.** J. J. van Laar [1] found a slight absorption whereby the metal acquires an electric charge, and H. Wislicenus stated that 10^{14} times less hydrogen is occluded by mercury than by copper. V. L. Chrisler also found that the press. in a hydrogen tube, fitted with a mercury anode and nickel cathode, fell from 2·41 to 2·365 mm. in 7 mins., and when **helium** is substituted for hydrogen, the decrease of press. is twice as great.

M. Berthelot could detect no sign of any reaction between **argon** or helium and mercury, nor could J. Stark detect any action of argon on mercury in a stream of canal rays. According to F. Fischer and F. Schröter, argon does not react with mercury when an arc with mercury as cathode and carbon as anode is made under liquid argon. A black cathode dust of mercury is formed.

O. Loew,[2] and I. Walz obtained a pasty mass by shaking zinc amalgam with a soln. of mercuric chloride containing platinic, palladous, or auric chloride. Air must be excluded, and the mixture kept cold. According to E. Duter, the electrolysis of water with a mercury cathode and platinum anode gives a pasty mass which gives hydrogen when the current is interrupted; and A. Potier observed similar phenomena in the electrolysis of a soln. of the nitrate. The product decomposes slowly when dried or when kept under water; and, according to O. Loew, the mercury loses 150 times its vol. of hydrogen, and the mass swells considerably during the evolution of the gas. It reduces ferric salts and ferricyanides, and decolorizes potassium permanganate. According to G. Meyer, and C. A. Seely there are no grounds for assuming this product is a *mercury hydride*. W. Duane and G. L. Wendt found that immediately hydrogen has been bombarded by α-radiations the gas is activated so that it reacts with mercury, forming yellow crystals of what may be mercury hydride—vide **1.** 7, 7. F. Paneth and co-workers observed no sign of the formation of a gaseous mercury hydride by the action of activated hydrogen. G. N. Lewis and R. F. Jackson deduced the existence of *hydrogen amalgam* from the behaviour of the mercury cathode during the separation of hydrogen in electrolysis.

A. Matthiessen and C. Vogt[3] found that no **oxygen** is absorbed by purified mercury, nor is the mercury affected by shaking it with **air** or oxygen; C. Christiansen, and J. M. Crafts found very little action when purified mercury is shaken with oxygen or air; and M. de Broglie detected some oxidation when the shaking is vigorous. J. Stark found that mercury takes up oxygen when exposed to the canal rays. E. Amagat found that at ordinary temp. no action occurs even at high press. if the oxygen be dry. M. Berthelot found mercury is superficially oxidized by oxygen or air, and the action is accelerated by the presence of acids; and D. Macaluso said that the oxidation occurs only in the presence of water vapour. According to H. B. Baker, mercury vapour, under ordinary circumstances, contains only atoms of mercury which exhibit little tendency to combine with oxygen. The vapour, however, is ionized in the mercury vapour lamp, and when the current is cut off and oxygen is admitted shortly afterwards, the mercury becomes covered with a layer of mercuric oxide. Since the temp. of the lamp is much below that at which ordinary mercury vapour combines with oxygen, it is evident that in this case ionization can bring about chemical action. The oxidation of heated mercury has been previously discussed—**1.** 1, 16; **1.** 8, 2.

According to L. Gmelin, when the two poles of Hare's deflagrator are made to dip into two vessels full of mercury, and the mercury allowed to run in a fine stream through a narrow opening from the upper to the lower vessel, visible combustion takes place. According to R. Hare, the blue light which is seen whenever the circuit of a powerful galvanic battery is closed by dipping the connecting wire into mercury, is likewise due to combustion of the mercury. C. F. Schönbein found that mercury acts in the presence of oxygen as a catalytic agent upon some colouring matters.

Oxygen free from ozone does not affect the mirror-like surface of mercury, but the latter is readily attacked by dry **ozone.** According to A. Volta, when a tube of mercury is brought in contact with dry ozonized oxygen, the meniscus instantly disappears, and the surface becomes quite plane; after a few minutes' contact with the ozone, however, the edges become depressed, and the meniscus again reappears with a clean surface, the convexity gradually increasing until it far exceeds the normal curvature; this lasts for a couple of hours, and then the meniscus returns to its ordinary state. This phenomenon the author believes to be electrical, the period of maximum convexity corresponding with the maximum polarity of the metal; this, as in the case of other metals, is negative, but there is no permanent deflection.

Analogous results are obtained with moist ozone, but they are much less strongly marked. According to A. von Antropoff, if ozonized oxygen be passed through mercury, the latter becomes pasty and appears like tin-amalgam. It has been stated that ozone reacts with mercury, forming mercurous oxide, Hg_2O. W. Manchot and W. Kampschulte's observations are indicated under ozone—**1**. 14, 6.

According to M. T. Lecco, **water** vapour is not decomposed by mercury. D. Macaluso found that air-free water-vapour does not affect mercury; but with a mixture of air and water-vapour oxidation takes place, with the production of the well-known grey pellicle of suboxide. This action is analogous to the formation of mercurous chloride when mercury is left in contact with gaseous hydrogen chloride or its aq. soln. in presence of air, whereas in pure hydrogen chloride, or its pure aq. soln. perfectly deprived of air, no such formation takes place. A. Wiggers,[4] and E. F. Anthon believed that mercury is slightly soluble in boiling water, because the liquid which is obtained by decantation from the mercury, when conc. by evaporation, gives the reactions of that element. C. Paton, and J. Girardin failed to detect mercury in water which had been boiled with that element; and L. Gmelin, and E. Riegel also showed that there is no foundation for assuming that mercury is soluble in water, because, when water is poured upon mercury, boiled down to one-half, decanted, then left to stand for several days, again decanted, and thrown upon a thick paper filter, small quantities of mercury, sufficient to silver gold-leaf, remain on the filter; but the filtrate, when mixed with nitric acid and evaporated, shows no trace of mercury. If C. Barfoed's statement be true that mercury can diffuse through a film of water at ordinary temp., the metal must be soluble in that menstruum. This is confirmed by A. Christoff's observation that mercury can dissolve in and diffuse through water which contains air, nitrogen, carbon dioxide, sulphuric acid, potassium hydroxide, and also through benzene, nitrobenzene, or alcohol. The diffusion of mercury was proved by the reduction of a soln. of auric chloride contained in a separate vessel. It was so shown that mercury left for a long time in contact with water suffers a slight loss in weight, although the amount of mercury retained by the water is too small to be detected. F. Fischer also made observations on the "chemical soln. press." of mercury. According to C. F. Schönbein, ozone—or is it hydrogen peroxide?—is formed when mercury is shaken with air and water, and on adding potassium iodide, a blue colour appears and potassium mercuric iodide is formed; and, added K. Voit, if sodium chloride is present, sodium mercuric chloride is formed and guaiacum tincture is coloured blue. The presence of mercury was found by W. van Rijn to accelerate the attack of iron, magnesium, and particularly aluminium on water, but not the attack by zinc or nickel. O. P. Watts and N. D. Whipple included mercury in their study of the action of various reagents on zinc—*q.v.*

C. F. Schönbein[5] found that guaiacum tincture is coloured blue by hydrogen peroxide in the presence of mercury. According to J. A. Kappers, and B. J. Boerrigter, when mercury is shaken with a soln. of **hydrogen peroxide,** the meniscus is flattened, and a film of black powder—a mixture of mercurous and mercuric oxides—is formed. T. Fairley found that the presence of hydrogen peroxide favours the dissolution of mercury in acids; and with hydrochloric acid, mercurous chloride is formed. When mercury is covered with a 10 per cent. soln. of purified hydrogen peroxide, a bronze-yellow film appears on the surface of the metal, and the development of oxygen begins. According to G. Bredig and co-workers—E. Wilke, and J. Weinmayr—the catalytic decomposition of hydrogen peroxide by mercury proceeds rhythmically with a regularly increasing and decreasing velocity. It is estimated that the minimum thickness of the surface film of active mercury is 3×10^{-8} cms. It is assumed that the **periodic reaction** is conditioned by the formation and decomposition of a film of what is probably mercurous oxide, for if agents which dissolve this oxide are present the pulsating action ceases—sodium sulphate or carbonate, potassium nitrate or chlorate act vigorously, acids, or potassium chloride or bromide act feebly. The optimum alkali addition is from

10^{-3} to 10^{-4} mol per litre. Temp. has a great influence; cooling increases the period of oscillation, warming makes the reaction aperiodic. Reducing the press. lessens, and illumination raises the activity. The addition of 4×10^{-5} to 2×10^{-5} mol of alkali chloride per litre paralyzes the action; sulphates retard the action; and nitrates have no influence. During the periodic action, the electrolytic tension of the mercury varies periodically. The theory of the action has been discussed by A. von Antropoff, E. Wilke, C. Fredenhagen, and T. Okaya. According to D. Borar, a soln. of **sodium dioxide** is not affected by mercury.

According to M. C. Schuyten,[6] the **halogen** in mercuric chloride, bromide, or iodide can be replaced by the other halogens even in the presence of an excess of the salt; the only exception is in the case of mercuric bromide and iodine, for the bromine is not displaced by the iodine. According to W. A. Shenstone, the presence of moisture is not necessary for the halogens to react with mercury. J. Schröder also found that the halogens are specially reactive with mercury salts dissolved in pyridine. The actions of **fluorine** and **hydrogen fluoride**; of **chlorine** and **hydrogen chloride**; of **bromine** and **hydrogen bromide**; and of **iodine** and **hydrogen iodide** on mercury, will be discussed in connection with the preparation of the corresponding mercury halides. G. Reboul showed that when chlorine is much diluted with an inert gas, and passed over mercury, no marked production of conducting ions occurs; and that the vapour of chlorine, bromine, or iodine, diluted with an inert gas, attacks a meniscus of mercury most vigorously where the curvature is greatest. K. Strzyzowsky has also made observations on the action of iodine on mercury. J. Schröder noted that the mercury formed by the action of pyridine on mercurous salts is immediately converted by iodine into mercuric iodide, which then passes into soln. R. Varet found mercury dissolves in a potassium iodide soln. of iodine, and, according to R. G. van Name and G. Edgar, in a potassium bromide soln. of bromine. R. S. Norris and F. G. Cottrell found that liquid hydrogen iodide rapidly dissolves mercury at ordinary temp. with the evolution of hydrogen and the formation of both iodides. According to W. Nernst, A. Harding, and F. Dolezalek, conc. **hydrochloric acid** dissolves mercury with the evolution of hydrogen; and, according to A. Harding, **hydrobromic acid** dissolves mercury. J. B. Hannay found that **iodine monochloride** forms mercuric chloride and iodide. J. J. Sudborough found that **nitrosyl chloride,** NOCl, and mercury, in a sealed tube, in the cold, form golden plates which decompose on opening the tube, furnishing mercuric chloride and nitrosyl chloride. According to P. Nicolardot, **sulphur dichloride,** S_2Cl_2, acts on mercury like hydrogen chloride, but if the attack is slow, mercury sulphide is formed; H. B. North found **thionyl chloride** does not act on mercury in the cold, but with a large excess, a few hours' heating at 150° furnishes mercuric chloride, sulphuryl chloride, and sulphur dichloride; with a small excess, mercuric chloride, sulphur dioxide, and sulphur dichloride; while, if the mercury is in excess, mercurous chloride, sulphur dioxide, and sulphur dichloride are formed; mercury and **sulphuryl chloride** in a sealed tube at 160°–180° furnish mercuric chloride and sulphur dioxide. J. A. Besson found **thionyl bromide** forms mercury bromide, sulphur dioxide, and sulphur, while **thionyl chlorobromide** forms mercurous bromide, thionyl chloride, sulphur dioxide and sulphur. E. Divers and M. Shimose found **selenium dichloride,** Se_2Cl_2, is decomposed by mercury. H. Moissan found that **phosphorous trifluoride** does not act on mercury at 350°. H. Goldschmidt found that mercury and **phosphoric chloride,** PCl_5, furnish mercuric chloride and phosphorous chloride, PCl_3. According to J. A. Besson, mercury decolorizes a soln. of **phosphorous iodide** in carbon disulphide, and mercury iodide is formed. B. Reinitzer and H. Goldschmidt heated an excess of mercury with **phosphoryl chloride,** $POCl_3$, for 15 hrs. at 290°, and obtained phosphorous chloride, phosphoric oxide, pyrophosphoryl chloride, $P_2O_3Cl_4$, crystals of mercurous oxide, and red mercury phosphide, while if the phosphoryl chloride be in excess, mercuric chloride and phosphate are formed. O. Ruff and co-workers found that **tungsten hexafluoride** attacks mercury, especially in the presence of hydrogen fluoride; **tungsten oxytetrafluoride,** WOF_4, attacks

mercury only when warm, or in the presence of moisture. According to G. Meyer, the salt condenses on the surface of mercury immersed in a soln. of **alkali chloride ;** but, according to I. Bhaduri, neither neutral nor alkaline soln. of alkali chlorides act on mercury. J. Müller observed the formation of sodium mercuric chloride when a soln. of sodium chloride is shaken with mercury. W. Palmaer observed that a soln. of potassium chloride or **potassium iodide** dissolves mercury in the presence of air. A. Ditte made a similar observation, and H. S. Hatfield found that the dis solution of mercury in an aq. soln. of mercuric and potassium iodides in the presence of air, is accelerated in sunlight if a trace of an iron salt be present. J. Shukoff found mercury is dissolved at the anode during the electrolysis of soln. of the **potassium bromide,** chloride, or iodide. According to C. Barfoed, and D. Vitali, an aq. soln. of **auric chloride** or **hydrochloroauric acid** absorbs mercury vapour and gold is produced ; the reaction is very sensitive in the absence of nitric acid. A soln. of **platinic chloride** acts similarly. W. Wolters found **hypochlorous acid** attacks mercury, forming mercurous chloride, or, according to A. J. Balard, mercuric oxychloride, while, according to I. Bhaduri, **hypochlorites** form mercuric oxide. I. Bhaduri found that soln. of **alkali chlorates** have no action on mercury. A. Ditte stated that mercury is attacked by **iodic acid.**

According to R. von Schrötter,[7] C. Brame, and M. Rosenfeld, when **sulphur** and mercury are heated together, the two elements unite to form mercury sulphide. Similar remarks apply to **selenium.** A. Baudrimont found that **sulphur chloride** converts mercury into mercurous and mercuric chlorides. U. Antony and G. Magri found liquid **hydrogen sulphide** has no action on mercury, and, according to M. Berthelot, hydrogen sulphide does not react with mercury at ordinary temp., nor at 100° if moisture be excluded ; but if oxygen be also present, mercurous sulphide is formed at ordinary temp.—the presence of moisture retards the reaction. G. Reboul observed that the attack by hydrogen sulphide on the mercury meniscus is fastest where the curvature is greatest. J. Milbauer found that the presence of mercury does not stimulate the reaction between sulphur and hydrogen. M. Berthelot found that mercury very slowly decomposes **hydrogen selenide** with the formation of mercurous selenide—the reaction is not completed in three years at ordinary temp. W. Palmaer found that a soln. of **sodium sulphide** slowly dissolves mercury in the presence of air. O. Brunck found that **sodium hyposulphite** reacts with mercury, forming mercuric sulphide. According to M. Berthelot, mercury is not attacked by a cold aq. soln. of **sulphur dioxide** even after many days' action, alone, or in the presence of hydrochloric acid or dil. sulphuric acid. E. Divers and T. Shimidzu stated that mercury is not chemically attacked by **sulphur trioxide** provided moisture is rigorously excluded ; the only phenomenon observable is the ready pulverization of the mercury after it has been shaken with the trioxide. C. M. van Deventer found that conc. **sulphuric acid** readily attacks mercury while the dil. acid has no action. Water-free **sulphuric acid** was found by M. Berthelot gradually to attack mercury, and if shaken at 20° for a couple of months, sulphur dioxide, mercuric sulphate, and a trace of mercuric sulphide are formed. A. Ditte said that only hot conc. sulphuric acid attacks mercury, forming sulphur dioxide, and J. R. Pitman, in opposition to C. Baskerville and F. C. Miller, found that conc. sulphuric acid at 25° does not attack moist or dry mercury, whether air be present or absent, and whether the acid be in excess or not. According to J. B. Hannay, hot conc. sulphuric acid forms a mixture of mercurous and mercuric sulphates, and if the mercury is completely dissolved, only mercuric sulphate is formed. He attributed the formation of mercurous sulphate to the reducing action of sulphur dioxide. C. Baskerville and F. C. Miller found that an excess of mercury with sulphuric acid of sp. gr. 1·84 forms sulphur dioxide and white crystalline mercurous sulphate, but at about 20° this compound is decomposed by the excess of acid. When a mixture containing an excess of acid is heated at 100° for 20 hrs., mercurous sulphate is obtained, and on heating at 150° for 2 hrs., a mixture of mercurous and mercuric sulphates is produced, containing 50 per cent. of

the former salt; as the temp. is raised, however, the amount of mercurous sulphate diminishes until, when mercury is added to the boiling acid, the product consists entirely of mercuric sulphate. When mercurous sulphate, or a mixture of this with mercuric sulphate, is heated with sulphuric acid, the amount of sulphur dioxide evolved is proportional to the quantity of mercurous salt present. No indication could be obtained of the liberation of hydrogen during the initial stages of the reaction, and no sulphide or free sulphur was produced. The acid is directly reduced by the metal, even at ordinary temp. No trace of hydrogen, sulphur, or sulphide was formed. The sulphuric acid does not act on mercury like it does on copper; and by the prolonged action of the acid, C. Baskerville obtained some mercurous sulphide. P. Braham stated that if the sulphuric acid contains a trace of nitric acid, mercurous hydrosulphate, $HgHSO_4$, is formed after about a year's contact with mercury. J. Tafel has shown that no hydroxylamine is produced when nitric acid acts on mercury in the presence of sulphuric acid, and the reaction has been discussed by W. D. Bancroft. E. Sulkowsky found that dil. sulphuric acid attacks mercury in the presence of hydrogen peroxide. S. W. J. Smith studied the action of a mixture of sulphuric and hydrochloric acids. A. Sieverts and P. Lueg studied the retarding effect produced by alkaloids in the action of sulphuric acid on mercury.

G. Meyer found that with soln. of **sulphates** there is a condensation of the salt at the surface of the mercury. W. R. E. Hodgkinson and N. E. Bellairs found that fused **ammonium sulphate** acts less energetically on mercury than on copper; W. Smith attributed the action to the formation of ammonium hydrosulphate, NH_4HSO_4. According to D. Borar, a hydrochloric acid soln. of **cupric sulphate** is reduced to cuprous chloride by mercury. E. Divers and T. Shimidzu found that when **pyrosulphuric acid** acts on mercury no effervescence occurs, provided the vessel is occasionally shaken to renew contact. As the action proceeds, mercurous sulphate slowly separates in the solid state. By using an acid containing much sulphur trioxide, the whole may become solid, and the action arrested in consequence. In any case, when the action has proceeded far, sulphur dioxide escapes freely from the liquid with slight effervescence. If the soln. of the mercury in the acid is poured into water, mercurous sulphate is precipitated, mixed with metallic mercury, and no sulphur dioxide is left. But the already solidified mercurous sulphate is not thus affected by contact with water. The dissolution of the mercury without evolution of gas is attributed to the great solubility of sulphur dioxide in fuming sulphuric acid, and the precipitation of mercury which occurs, when the fuming acid soln. of mercury is treated with water, is due to the action of sulphur dioxide on mercurous salts. According to N. Tarugi, **persulphates,** in acid, neutral, or alkaline soln., attack mercury—the potassium salt less tardily than the ammonium salt—and, according to M. G. Levi, E. Migliorini, and G. Ercolini, the mercury is covered by a yellow powder of mercuric oxide or basic sulphate. According to D. Borar, when a cold soln. of potassium persulphate is shaken with mercury, a slight black precipitate is first formed, and then a white precipitate which slowly changes to a lemon-yellow colour. The soln. acquires an acid reaction, and it contains potassium sulphate. With hot soln. a yellow precipitate is formed almost immediately. Mercuric sulphate readily gives the yellow basic sulphate when treated with water, while mercurous sulphate, even on boiling does not do so. The suggested reactions are symbolized: $2K_2S_2O_8+2H_2O=4KHSO_4+O_2$; $4KHSO_4+O_2+2Hg=2K_2SO_4+2HgSO_4+2H_2O$; and $2HgSO_4+3H_2O=H_2SO_4+HgSO_4.HgO.2H_2O$. When mercury is heated with **selenic acid,** H_2SeO_4, W. C. A. Cameron and E. W. Davy found a mixture of mercurous and mercuric selenite, but if the selenic acid be in excess, mercuric selenate is produced. According to M. E. Pozzi-Escot, a trace of **sodium tungstate** in conc. hydrochloric acid produced a blue coloration in the presence of mercury. A. Chilesotti found that the mercury cathode is not suitable for reducing **molybdates.**

According to F. Emich, a mixture of sulphuric acid and **sodium nitrite** reacts

with mercury, forming nitric oxide, and the velocity of the reaction is proportional to the surface presented by the mercury; while P. Sabatier found that when mercury is shaken with sulphuric acid and sodium nitrite, blue nitrosodisulphonic acid is formed. According to F. Raschig, **nitrososulphonic acid** or nitrosulphuric acid, $ONO.HSO_3$ or $NO_2.HSO_3$, in the presence of conc. sulphuric acid, is reduced by mercury to what he regards as blue nitrososulphonic acid, $NO(OH)HSO_3$, or what E. Divers regards as nitroxysulphuric acid, $HO.NO_2 : N.HSO_3$, and then to nitric oxide and sulphuric acid; E. Divers represents the reaction differently: $2Hg+ONO.HSO_3+NO.SO_4=Hg_2SO_4+HO.NO_2 : N.HSO_3$; and O. Wentzky interprets the reaction still another way. W. Manchot also noted the reduction, by mercury, of the blue-coloured **nitroxysulphuric acid,** $NO.NO_2 : N.HSO_3$, produced in the manufacture of sulphuric acid.

F. H. Newman [8] studied the effect of **nitrogen** on mercury as cathode in a discharge tube. Mercury can be agitated for a long time with nitrogen without change, and M. Berthelot could detect no reaction between the two elements. M. de Broglie found that nitrogen is ionized when bubbled through mercury. According to J. Stark, nitrogen is absorbed by mercury in a stream of canal rays. R. J. Strutt found activated nitrogen reacts with mercury, forming mercury nitride. W. Weyl, and E. C. Franklin and C. A. Kraus stated that mercury is not soluble in liquid **ammonia,** but W. Weyl found that sodio-ammonium and mercuric amminochloride react to form **mercury diammine,** $Hg(NH_3)_2$, as in the case of zinc ammine. C. Matignon and G. Desplantes found mercury is oxidized when shaken with aq. ammonia in the presence of oxygen. J. McKay found that when a soln. of **hydroxylamine** is electrolyzed with mercury electrodes, it forms ammonia. P. Sabatier and J. B. Senderens found that mercury is not perceptibly oxidized at 450° in **nitric oxide;** W. Ramsay found **nitrogen peroxide** to be decomposed by mercury; C. F. Gerhardt obtained mercuric nitrate and nitric oxide by passing nitrogen peroxide through cold mercury; and E. Divers and T. Shimidzu represented the reaction: $Hg+N_2O_4=HgNO_3+NO$, and showed that a little mercuric nitrate but no nitrite is formed. F. Russ found that nitrogen peroxide has no appreciable action on mercury at low temp. G. Reboul found that **nitrogen trioxide** attacks a meniscus of mercury fastest where the curvature is greatest.

E. Divers likened the action of **nitric acid** and **nitrous acid** on mercury to that of the same acids on copper—*q.v.* E. Abel found cold 0·3*N*-HNO_3 has no perceptible action on mercury. According to N. A. E. Millon, purified nitric acid acts on mercury only when a reducing agent is present, and V. H. Veley, and E. Divers showed that nitric acid freed from nitrous acid does not attack mercury; and J. H. Stansbie found that the speed of the reaction is dependent on the proportion of nitrite which is present; and is decreased when the nitrite is converted to nitrate by boiling. W. Reuss obtained only mercurous nitrate by the action of dil. nitric acid on mercury in the cold, and also when heated on a water-bath provided the conc. of the nitric acid does not fall below 4 per cent. nor rise above 20 per cent. HNO_3. According to P. C. Ray, when mercury is covered by a 10-cm. layer of nitric acid, of sp. gr. 1·11 at 15°, and at a temp. of 30°–35°, bright yellow crystals of mercurous nitrite are freely formed. A part of the nitric acid is reduced to nitrous acid; some of the nitrite is decomposed by the nitric acid, and the proportion of nitrous acid in the soln. rapidly increases until mercurous nitrite and nitrate are accumulating in equi-molecular proportions; the proportion of nitrous acid in the soln. then remains constant and acts as a catalytic agent in the reaction between mercury and nitric acid: $2Hg+2HNO_3=HgNO_2+HgNO_3+H_2O$. He further assumes that when dil. nitric acid and mercury are left in contact for a long time, the following nine salts may form: (1) $Hg_2(NO_2)_2$; (2) $Hg_2(NO_3)_2$; (3) $Hg_2(NO_3)_2.2H_2O$; (4) $HO.Hg_2.NO_3$; (5) $Hg_2(NO_3)_2.HO(NO_3)Hg_2$; (6) $Hg_2(NO_3)_2.4HO(NO_3)Hg_2$; (7) $HgO.2HO(NO_3)Hg_2$; (8) $HgO.HO(NO_3)Hg.HO(NO_3)Hg_2$; and (9) $Hg(NO_3)_2$ aq.; not all of these salts have been isolated. According to C. Montemartini, mercury yields no ammonia with 27 and 50 per cent. nitric acid; the quantity of nitric

oxide produced diminishes as the conc. increases; 27·5 per cent. acid gives no nitrogen peroxide, but stronger acid yields large quantities just as in the cases of copper and bismuth. Mercurous nitrate is obtained in soln. on operating with 25 per cent. acid; more conc. acid (50–70 per cent.) gives the mercuric salt. T. Ericson-Aurén attributed the activity to action of local couples, with hydrogen as depolarizer.

J. J. Acworth found that in the presence of ammonium nitrate, nitrogen is the chief product of the reaction between mercury and nitric acid. N. A. E. Millon, V. H. Veley, and P. C. Ray showed that the presence of ferric sulphate or nitrate removes nitrous acid from nitric acid as fast as it is formed, and it thus inhibits the chemical change between nitric acid and the metals. P. C. Ray found that the reaction between mercury and nitric acid is accelerated by manganese or sodium nitrate, while the sulphates of manganese, sodium, and potassium neither accelerate nor retard the action. B. C. Banerji and N. R. Dhar found that while the presence of ferrous sulphate accelerates the action of nitric acid on mercury, the presence of ferric nitrate, sodium nitrate, manganous nitrate, potassium chlorate, or potassium permanganate retards the action. P. Ménière removed the vapour of mercury from air by passing the contaminated air through boiling nitric acid. W. Zorn obtained hyponitrites, hydroxylamine, and ammonia in the *electro-reduction of nitric acid* with a mercury cathode; and J. Tafel obtained an almost quantitative yield of hydroxylamine. W. J. Müller, with an amalgamated copper cathode, obtained nitrites and ammonia during the electro-reduction of soln. of **nitrates.** J. Shukoff obtained mercurous and mercuric salts in the proportions 120 : 1 in the electrolysis of a soln. of **potassium nitrate.** D. Borar observed no reaction between mercury and an aq. soln. of potassium nitrate. G. Meyer stated that with aq. soln. of the nitrates some of the salt condenses at the surface of the mercury. W. R. E. Hodgkinson and co-workers observed no reaction between mercury and aq. soln. of **ammonium nitrate,** but the molten salt was found to attack mercury less energetically than copper, the attack, according to W. Smith, is a result of the formation of nitric acid from the ammonium nitrate. W. R. E. Hodgkinson and A. H. Coote found that fused **ammonium nitrite** has no action on mercury.

The affinity between mercury and **phosphorus** appears to be small. According to O. Emmerling,[9] and A. Granger, phosphorus vapour does not react with mercury vapour either at atm. press. or under press. in a sealed tube. A. Stock and F. Gomolka assume that phosphorus crystallizes from its soln. in molten mercury. D. Gernez found that molten phosphorus dissolves mercury, forming a colourless liquid which blackens on cooling owing to separation of mercury; the soln. clears again if re-heated. M. Blondlot found that mercury catalyzes the change from ordinary to black phosphorus. Mercury appears to form amalgams with **arsenic, antimony,** and **bismuth,** but the evidence in the case of arsenic and antimony is not so satisfactory. H. J. S. Sand and J. E. Hackford reduced solns. of **arsenates** and **arsenites** to arsenic, but not to arsine, by electrolysis between mercury electrodes. T. F. Rutter found that with the mercury cathode **vanadates** are reduced to vanadium sulphate, VSO_4, in the presence of sulphuric acid.

O. Ruff and B. Bergdahl[10] state that the solubility of **carbon** in mercury is very small. H. Erdmann and P. Köthner found that the metallic lustre of mercury is not altered by heating it with **acetylene,** but at the distillation temp. of mercury, a very small grey sublimate is formed which gives a scarcely perceptible trace of acetylene when treated with water. M. Berthelot stated that when mercury is heated to 550° in a sealed tube with **carbon monoxide,** the weight of the mercury increases a little, no free carbon can be detected, but a trace of carbon dioxide is formed. The prolonged shaking of mercury with **carbon dioxide** gives no perceptible sign of any chemical change; but with a prolonged sparking, T. de Saussure found that some mercuric oxide is formed. M. Berthelot found that cyanogen does not unite with mercury when heated in a sealed tube at 200° or 300°; the gas does not appear to be absorbed by the mercury, but the latter is covered with a brown film.

E. Obach found that purified **carbon disulphide** as well as that containing hydrogen sulphide as impurity, acts on mercury in the presence of air. According to M. Berthelot, when a mixture of nitrogen and carbon disulphide confined over mercury is sparked, or exposed to the silent discharge, mercuric thiocyanate, $Hg(SCy)_2$, is formed. H. Moissan noted that **ethylene tetraiodide** acts slowly on cold mercury. G. Tammann found mercury vapour reacts with **carbon tetrachloride** at 600°–700° producing a dense form of carbon and mercurous chloride. The reaction starts at 400° when the press. is 900–2760 atm. Analogous results were obtained with **carbon tetrabromide,** and **carbon tetraiodide**—*vide* sodium amalgam. According to L. Elsner, mercury is insoluble in an aq. soln. of **potassium cyanide ;** but W. Palmaer found it to be slowly soluble with access of air ; and G. A. Goyder observed a marked solubility without the evolution of gas in a 6 per cent. soln. of that salt. A. Brochet and J. Petit found that the alternating current electrolysis of a soln. of potassium cyanide with mercury electrodes yields no double salt ; but B. Renault found some mercury dissolves at the anode during the direct current electrolysis of the soln. G. McP. Smith found a soln. of **potassium ferricyanide** dissolves mercury best in the presence of potassium hydroxide, and he represents the reaction : $16K_3FeCy_6+6Hg=6K_2HgCy_4+Fe_4(FeCy_6)_3+9K_4FeCy_6$; or with potassium hydroxide : $Fe_4(FeCy_6)_3+4Fe(OH)_3$. G. Meyer found that potassium ferricyanide is reduced by mercury to the ferrocyanide. A. Brochet and J. Petit did not succeed in electrolyzing a soln. of **potassium ferrocyanide** with mercury electrodes.

According to A. Christoff, mercury does not dissolve in **alcohol, benzene,** or **nitrobenzene,** although the vapour can diffuse at ordinary temp. through these liquids. H. C. Bolton found that mercury dissolves in a mixture of **citric acid** and sodium nitrate ; and J. H. Mathews, that **trichloroacetic acid** in nitrobenzene soln. does not attack mercury. C. B. Gates studied the displacement of copper by mercury from soln. of salts of the organic acid in various organic solvents. Mercury acts as a catalytic agent in the reduction of some organic compounds—*e.g.* D. Borar found that a little nitrobenzene is reduced to aniline in the presence of mercury and hydrochloric acid ; several organic compounds are reduced electrolytically with a mercury cathode ; and many organic sulphides act on mercury. According to D. B. Dott, purified **ether** has no action on mercury, but ether containing peroxide impurities produces a dark film, and a grey powder ; and if much peroxide is present, some yellow mercuric oxide.

Mercury was found by C. Winkler [11] not to unite with **silicon,** even if the two elements are heated for a day at 300°. F. Grandjean found mercury is absorbed by some **zeolites**—*e.g.* **levyne** and **chabasite,** but not by **gmelinite.** E. Warburg observed in the electrolysis of **glass** between mercury electrodes—not with electrodes of sodium amalgam—the formation of a badly conducting layer. G. Schulze noted the diffusion of mercury in the glass. V. Meyer found that in the distillation of impure mercury, glass retorts are soon destroyed, but not so porcelain retorts. According to H. Moissan, **boron phosphide,** BP, does not act on mercury ; **boron trisulphide** has no action on mercury, but **boron pentasulphide** is reduced to the trisulphide ; **boron phosphoiodides**—BPI_2 at 100°, and BPI in carbon disulphide soln.—are reduced to the phosphide, BP. According to O. Mohr, and E. von Pickardt and W. Angermann, vessels of **aluminium** are rapidly attacked by mercury. A. Holt found that sodium hydride is not affected by mercury. A. Matthiessen and C. Vogt stated that mercury does not dissolve **mercuric oxide,** but C. Barfoed found that by trituration mercury can form a salve-like mixture with **mercurous oxide** and **mercurous iodide,** and that the oxides of other heavy metals, like **lead oxide,** behave in a similar way. H. Rose stated that mercury precipitates metal oxides from many **metal salt** soln., and A. Mailhe added that basic salts are also precipitated. D. Borar found that **ferric salts** in the presence of hydrochloric acid are not reduced by mercury. P. Schafhäutt found that mercury reduces aq. soln. of ferric chloride, forming mercurous and ferrous chlorides ; the action is faster in the presence of hydrochloric acid. The observation was verified by D. J. Carnegie,

and L. W. McCay and W. T. Anderson. According to D. Borar, **potassium dichromate** is reduced under these conditions: $K_2Cr_2O_7+6Hg+14HCl=6HgCl+2CrCl_3+2KCl+7H_2O$; he also represented the reduction of **potassium permanganate** by mercury: $2KMnO_4+3Hg+H_2O=3HgO+2MnO_2+2KOH$; and W. Kirchmann stated that the reduction in the cold gives mercurous oxide, and when heated, mercuric oxide. Aq. soln. of alkali permanganates and mercury were found by A. Gawalowsky to form gradually a deep violet compound, and, in the presence of potassium hydroxide, a double manganate is formed together with a black substance, possibly mercurous manganate. F. Streintz found that at 100°, the vapour of mercury forms a mirror-like coating on the faces of crystals of **argentite,** or silver glance, Ag_2S, and some cinnabar, HgS, is simultaneously formed. The action of mercury on the metals is discussed in connection with the respective amalgams. A. Feodoroff found that when mercury is heated in an hermetically sealed **iron** tube, the latter is permeable to the former at 600°–620°. A sq. metre of surface of mercury was found by H. von Euler to absorb 0·0004 mgrm. of ions from a soln. of **mercuric chloride.**

Reactions of analytical interest.—There are two series of mercury salts—mercurous salts, and mercuric salts. In general, heat and light transform mercurous salts—nitrate, chloride, phosphate, acetate, sulphate, etc.—into mercuric salts and mercury, while the reverse change may occur at lower temp. **Hydrochloric acid** and **soluble chlorides** give no precipitate with mercuric salts of moderate conc., but with mercurous salts, a white precipitate of mercurous chloride is formed, which is insoluble in water and dil. acids, but soluble in conc. nitric acid or in aqua regia, and in chlorine or bromine water, $2HgCl+Br_2=HgCl_2+HgBr_2$. If the soln. of the mercurous salt is conc. the precipitate is curdy, if dil. the precipitate is pulverulent, and if very dil., a white opalescence is produced which, according to C. H. Pfaff,[12] is visible with soln. containing one part of mercurous nitrate in 100,000 parts of water; C. R. Fresenius said 1 in 327,000; and F. Jackson, 1 in 16,000 with hydrochloric acid and 1 in 15,000 with sodium chloride soln. When mercurous chloride is boiled for a long time with water, it becomes grey owing to its partial decomposition into mercury and mercuric chloride, and when boiled with sulphuric acid, sulphur dioxide is evolved: $2HgCl+H_2SO_4=2HCl+Hg_2SO_4$, followed by $Hg_2SO_4+2H_2SO_4=2H_2O+2HgSO_4+SO_2$. Mercurous chloride is blackened by alkali hydroxide, and by aqua ammonia; and it is slowly dissolved by cold soln. of ferric salts, chromic acid, and permanganic acid, forming mercuric salts. **Hydrobromic acid** and **soluble bromides** also give white precipitates with mercurous salts. Mercurous salts give an olive-green precipitate of mercurous iodide when treated with a soln. of **potassium iodide;** the precipitate is soluble in an excess, forming mercuric potassium iodide, K_2HgI_4, and mercury. Mercuric salts give a red precipitate of mercuric iodide which is soluble in an excess, forming the double salt, K_2HgI_4—cadmium salts behave similarly. According to F. Jackson, one part of a mercurous salt in 8000 can be detected and one part of a mercuric salt in 2000; for the latter, T. G. Wormley gave 1 : 3380, and P. Jannasch 1 : 1500.

When soln. of mercuric salts are treated with **hydrogen sulphide,** a white precipitate of mercuric thiochloride, $HgCl_2.2HgS$, is first formed; this is coloured yellow, brown, and finally black by the prolonged action of hydrogen sulphide. According to R. Palm, a soln. of mercuric cyanide does not give these intermediate compounds, but the black sulphide is precipitated directly. A. Kekulé found that hydrogen sulphide does not precipitate the sulphide from soln. of mercuric iodide in hydriodic acid, and similar remarks apply to soln. of mercuric bromide in hydrobromic acid. R. Rupp found that the mercury is slowly precipitated from a soln. of mercuric salicylate. According to J. L. Lassaigne, one part of mercuric salt can be detected in 23,000 parts of soln.; T. G. Wormley said 1 in 6770; and F. Jackson, 1 in 16,000. The sensitiveness of the reaction has also been examined by F. C. Schneider, B. Neumann, and by L. Vignon. Black mercuric sulphide is insoluble in boiling dil. acids. It dissolves in conc. hydrochloric acid. Hot conc. nitric acid gradually changes it

into white thionitrate, $Hg(NO_3)_2.2HgS$, and by a longer action, soluble mercuric nitrate is produced. The sulphide dissolves readily in aqua regia with the separation of sulphur; it is insoluble in soln. of potassium or sodium hydroxide, and ammonium sulphide, but, unlike the sulphides of silver, lead, bismuth, and copper, it dissolves readily in soln. of the alkali sulphide—not, according to C. Barfoed, hydrosulphide—forming, say, $Hg(SK)_2$, which is readily hydrolyzed by water: $Hg(SK)_2+H_2O \rightleftharpoons KOH+KSH+HgS$, so that a large excess of the alkali sulphide is needed for the soln. Unlike the sulphides of silver, lead, bismuth, copper, and cadmium, mercuric sulphide dissolves in potassium thiocarbonate soln., and from the soln. it is precipitated by carbon dioxide. According to K. Bülow, in the presence of zinc or cadmium sulphide, a soln. of sodium sulphide converts mercuric sulphide into a double sulphide; while, according to T. Willm, mercuric sulphide is perceptibly soluble in ammonium sulphide in the presence of stannic sulphide. With mercurous salts, hydrogen sulphide precipitates immediately a black mixture of mercuric sulphide and mercury; the latter remains undissolved when the precipitate is treated with potassium sulphide, but it all dissolves in an alkali polysulphide. J. L. Lassaigne found that one part of mercurous salt in 46,000 parts of soln. can be detected by hydrogen sulphide. J. Haidlen and C. R. Fresenius found that hydrogen sulphide gives a precipitate with mercuric salts in the presence of potassium cyanide; and C. J. Pretzfeld, in the presence of tartaric acid. According to J. W. Slater, a soln. of **sodium sulphide,** or of **ammonium sulphide**, behaves like hydrogen sulphide.

According to J. F. John, and H. Rose, a soln. of **potassium hydroxide** precipitates black mercurous oxide, Hg_2O, mixed with some mercuric oxide and mercury, from soln. of mercurous salts; and from mercuric salts, yellow mercuric oxide. If insufficient alkali is added for complete precipitation, a reddish-brown basic salt, say, $HgO.HgCl_2$, or $2HgO.HgCl_2$, is formed, and, in the presence of ammonium salts, the so-called white precipitate, say, $NH_2.Hg.O.Hg.NO_3$, is formed. Mercuric oxide and the basic salts are readily soluble in acids; but not in an excess of the precipitant. J. Spiller found that in the presence of citric acid no precipitation occurs; but C. Aubel and G. Ramdohr found that tartaric acid does not prevent the precipitation. F. Jackson found one part of mercuric salt in 500 parts of water could be detected by sodium hydroxide; T. G. Wormley said 1 : 677. Aq. **ammonia** with mercurous nitrate gives a black mixture of mercury and a mercuric amido-salt, say, $NH_2.Hg.O.Hg.NO_3$; with mercurous chloride, a mixture of mercury and mercuric amidochloride, $Cl.Hg.NH_2$, is formed. When the black precipitate is boiled with dil. hydrochloric acid, or a conc. soln. of ammonium chloride, the amide passes into soln. and the mercury remains undissolved. N. T. de Saussure, and C. H. Pfaff stated that 0·000006 part of ammonia in one part of water gives a sensible coloration with mercurous nitrate. The reaction has also been discussed by H. Hager. Aq. ammonia gives with mercuric chloride a white precipitate, $Cl.Hg.NH_2$, the so-called infusible white precipitate; this precipitate is soluble in acids, and in hot ammonium chloride, forming a fusible white precipitate, $Hg(NH_3Cl)_2$. When aq. ammonia is allowed to act on mercuric nitrate, the white compound, $NH_2.Hg.O.Hg.NO_3$, is formed which is easily soluble in ammonia in the presence of ammonium nitrate. T. G. Wormley found that one part of mercuric salt in 13,500 parts of water can be detected by the ammonia reaction; and F. Jackson, one part of mercurous or mercuric salt in 80,000 of soln. Soln. of mercuric chloride or nitrate give a reddish-brown precipitate of a basic carbonate, $3HgO.HgCO_3$, when treated in the cold with **alkali carbonate;** when boiled, yellow mercuric oxide is formed. Alkali carbonates with mercurous salts precipitate yellow mercurous carbonate which quickly becomes grey owing to the decomposition: $Hg_2CO_3=HgO+Hg+CO_2$. Similar results are obtained with **ammonium carbonate** as are obtained with aq. ammonia. F. Jackson found the sensitiveness of the reaction with sodium carbonate to be 1 : 1600 with mercurous salts, and 1 : 250 with mercuric salts. According to H. Demarçay, cold soln. of mercurous or mercuric salts are precipitated by

magnesium, barium, strontium, or calcium carbonate. A soln. of mercuric chloride gives no precipitate with **alkali hydrocarbonates,** but a reddish-brown basic carbonate is obtained with soln. of mercuric nitrate. A soln. of **potassium cyanide** gives no precipitate with a soln. of mercuric chloride because both the cyanide and chloride readily form soluble complexes with alkali chloride or cyanide. Mercuric nitrate gives a white precipitate of mercuric cyanide which is soluble in an excess of water or of potassium cyanide. A soln. of potassium cyanide gives a mixed precipitate of mercury and mercuric cyanide when added to a soln. of mercurous nitrate. Mercuric nitrate soln. with **potassium thiocyanate** precipitate white mercuric thiocyanate soluble in an excess of either reagent; mercurous salts give a mixture of mercury and mercuric thiocyanate. Soln. of mercurous salts give a black precipitate of the sulphide when treated with **sodium thiosulphate;** and with mercuric salts, H. Rose obtained a white precipitate which redissolves in an excess of thiosulphate; the white precipitate slowly becomes yellow, and then brown; in a boiling feebly acid soln., the yellowish-orange precipitate rapidly forms black mercuric sulphide. Mercurous salts with **potassium ferrocyanide** give a white precipitate; mercuric salts also give a white precipitate, if not too dil., and the colour turns blue on standing for some time. Mercurous salts with **potassium ferricyanide** give a yellowish-green precipitate which becomes white on standing; and with mercuric salts a green precipitate. Mercurous salts give a white precipitate of mercurous phosphate when treated with **sodium phosphate,** sensitive, according to C. H. Pfaff, to 1 : 10,000; with mercuric salts, white mercuric phosphate is similarly precipitated, and the reaction, according to C. H. Pfaff, is sensitive to 1 : 500.

Not too dil. soln. of mercurous salts give a white precipitate of mercurous sulphate, Hg_2SO_4, when treated with **sulphuric acid** or a **soluble sulphate;** the precipitate is sparingly soluble in cold water, decomposed by boiling water, soluble in nitric acid, and blackened by alkalies. According to T. G. Wormley, the reaction is sensitive to 1 : 1000. Mercuric salts give no precipitate with sulphuric acid or soluble phosphates. Mercurous nitrate soln. gives a red precipitate of mercurous chromate when heated with a neutral soln. of **potassium chromate;** with mercuric salts, yellow mercuric chromate is precipitated, and this precipitate becomes red when mixed with water and allowed to stand for a long time, or boiled. F. Jackson found the sensitiveness of the reaction to be 1 : 4000 with mercurous salts, and 1 : 333 with mercuric salts. Mercuric nitrate soln. give a yellowish-brown precipitate with **alkali dichromate,** but not so with a mercuric chloride soln.; with mercurous salts, the red chromate is precipitated. A boiling soln. of **ferrous sulphate** reduces mercuric nitrate to the metal, but mercuric chloride or cyanide is not reduced; with mercurous salts, white mercurous sulphate is precipitated, and this, especially when heated, is reduced to the metal—not so with the mercurous halides. A soln. of **stannous chloride** reduces mercuric chloride first to insoluble mercurous chloride, and the latter in turn to the metal. If the grey powdered mercury be decanted from the soln., and boiled with dil. hydrochloric acid, globules of mercury are formed. F. Jackson found the sensitiveness of the reaction with stannous chloride to be one part of mercuric salt in 32,000 parts of soln., or one part of mercurous salt in 16,000 parts of soln., or, according to T. G. Wormley, 1 : 13,500. The metals **aluminium, copper, zinc,** and **iron** reduce mercurous and mercuric salts to mercury. C. Reichard gave the sensitiveness of the aluminium precipitation as 1 : 130,000; soln. of mercurous salts with **oxalic acid,** or **alkali oxalates** give a white precipitate of mercurous oxalate, $Hg_2C_2O_4$, sensitive, according to C. H. Pfaff, to 1 : 10,000; mercuric salts, excepting the chloride, also give a white precipitate, HgC_2O_4. According to P. Cazeneuve, mercurous and mercuric salts in alcoholic soln. give a bluish-violet coloration with **diphenylcarbazide;** the presence of copper masks the reaction, and the presence of zinc acts as an inhibitor. P. Ménière found the reaction sensitive to 1 : 5,000,000. According to G. Dèniges, **zinc purpurate** gives a peach-coloured precipitate with a soln. containing 0·4 mgrm. of mercury per c.c. Silver salts give a violet precipitate.

The uses of mercury.—Mercury is used in the amalgamation processes for the extraction of gold and silver; as an electrode in the preparation of normal cells, and in electroanalyses; in thermometers, barometers, and other physical and electrical apparatus. It is used in the preparation of mirrors.[13] Mercury arc lamps are used for illumination, and as a source of ultra-violet light. The salts are used as antiseptics, and in medicinal preparations; in photography; in the preparation of colours—*e.g.* vermilion; in organic syntheses, and in general chemical operations. The recovery of mercury from mercurous sulphate residues has been discussed by M. Lemire.

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§ 5. The Atomic Weight and Valency of Mercury

The ratios of the two sp. hts., and the vapour density of mercury vapour, previously discussed agree with the assumption that the mol. is monatomic, and I. Traube [1] cited evidence that the element has the same **molecular weight** in the liquid and gaseous states; and he found the **atomic solution volume** of 200·4 parts of mercury is the same as that of one part of hydrogen. The sp. ht. and heat of vaporization were found by M. Langlois to agree with the assumption that the mol. is monatomic. The effect of temp. on the sp. ht. led L. Sohncke and the sp. gr. before and after melting led C. A. Seyler to the same assumption. W. Broniewsky observed no signs of molecular association when mercury is cooled to −183°. J. Stark suggested that liquid mercury may have polyatomic molecules because the liquid is a good electrical conductor, while the vapour is an insulator. C. Liebenow also assumed from a comparison of the electrical conductivity of the metal and its amalgams that the molecule of liquid mercury is polyatomic. D. Strömholm found the rise of the b.p. of mercury chloride in ethereal soln. agrees with a mol. wt. of 277—theory for $HgCl_2$ requires 271. F. M. Raoult, J. J. van Laar, and G. Tammann, from the f.p. of amalgams assumed that the mol. is polyatomic; and R. Cenac inferred from Eötvös' rule that the molecule of liquid mercury is probably triatomic. A. Avogadro supposed that the mercury molecule is diatomic, and in that case, J. B. A. Dumas' value for the vapour density of mercury would make the mol. wt. of mercury 200, and the at. wt. 100, and the accepted formula HgO for mercuric oxide would have to be changed to Hg_2O. Independent evidence obtained by studying the chemical transformations of the mercuric compounds favours the formula HgO, and the assumption that the mol. of mercury vapour is monatomic. A. Kundt and E. Warburg's work on the sp. ht. of mercury vapour gives a value in harmony with M. A. Gaudin's early assumption that the molecule is monatomic.

The **valency** of mercury in mercurous salts is like that of silver, and in mercuric salts like that of zinc and cadmium. The hydrogen eq. of the former is 200, that of the latter, 100. J. Stark and co-workers state that the spectral lines 365·0 and 365·5 are produced by bivalent mercury ions, and the line 253·6, by univalent mercury ions. E. Abel, A. Ogg, and E. Bose believe that in aq. soln. mercurous ions are bivalent; W. Bolton obtained evidence of the formation of univalent ions in the electrolysis of soln. of mercuric halides in the alkali halides. J. von Kowalsky observed that mercury vapour in a high vacuum ionizes in two stages. J. J. Thomson observed in his positive ray analysis tube that the mercury atom may carry

1 to 7 and probably 8 electrostatic charges. E. Abel found the tendency of electrically neutral ions to pass into mercurous ions is greater than with the nobler mercuric ions. K. A. Hofmann and E. C. Marburg discussed the tendency of mercury to form atomic complexes ; and H. Ley and H. Kissel, the tendency to form Hg.C- and Hg.N-complexes.

J. J. Berzelius [2] represented mercurous and mercuric oxides respectively by the formulæ HgO and HgO_2 on the assumption that if the **atomic weight** of oxygen is 16, that of mercury is 400, but in 1826 he altered this to 200, making the formulæ the same as those employed at the present day. L. Gmelin represented the eq. wt. of mercury by 100, and the two oxides respectively Hg_2O and HgO. The value 200 for the at. wt. of mercury is supported by the inference from (1) Avogadro's rule applied to the vapour density, and the mol. wt. of the compounds in soln. ; (2) Dulong and Petit's rule ; (3) Mitscherlich's rule and the isomorphism of mercuric, lead, and cupric compounds ; and (4) the position of mercury in the periodic table. The latter has been discussed by A. J. Hopkins, R. Lorenz, F. Sanford, E. W. Wetherell, P. C. Ray, C. Zenghelis, G. Tammann, A. Smits and H. L. de Leeuw, etc.

In 1818, N. G. Sefström [3] determined the at. wt. of mercury by oxidizing the heated metal, and obtained the value 200·9. In 1833, E. Turner decomposed mercuric oxide, and thus obtained the ratio HgO : Hg, from which the at. wt. is 200·6 ; O. L. Erdmann and R. F. Marchand, in 1844, obtained from the same ratio, 200·10 ; G. B. Taylor and G. A. Hulett reduced mercuric oxide with iron, and obtained $200{\cdot}37 \pm 0{\cdot}024$; and in 1896, W. L. Hardin evaluated the ratio HgO : Hg by the electrodeposition of mercury from a soln. of the oxide in a soln. of potassium cyanide, and he obtained 200·19. O. L. Erdmann and R. F. Marchand distilled the sulphide with copper, and from the ratio HgS : Hg obtained 200·54 for the at. wt. of mercury. E. Turner analyzed the chloride, and from the ratio $HgCl_2$: 2AgCl he calculated the at. wt. 202·05 ; and from the ratio HgCl : AgCl, 200·6. E. Turner also evaluated the ratio $HgCl_2$: Hg, by reducing mercuric chloride with stannous chloride, and obtained 199·6 ; L. F. Svanberg distilled mercuric chloride with lime, and from the ratio $HgCl_2$: Hg obtained 199·59 ; N. A. E. Millon by a similar method obtained 200·21 ; and W. L. Hardin, from the electrolysis of soln. of silver chloride, bromide, and cyanide in potassium cyanide, obtained from $HgCl_2$: Hg, 200·04 ; $HgBr_2$: Hg, 199·89 ; and $HgCy_2$: Hg, 199·99. C. W. Easley reduced mercuric chloride with hydrogen peroxide, and obtained 200·478 ; and by reducing the bromide, C. W. Easley and B. F. Braun obtained 200·64. W. L. Hardin also determined the electrochemical eq. of mercury in terms of silver, and from the ratio Hg : 2Ag obtained 200·02. G. Hinrichs, F. W. Clarke, and B. Brauner have attempted to deduce the best representative value for the at. wt. of mercury from these determinations. The value 200·6 is given in the International Table of Atomic Weights for 1921. A. L. Bernoulli calculated 200·817 from the kinetic theory. The **atomic number** is 80.

With the positive ray analysis, F. W. Aston found that mercury has about six **isotopes** with at. wt. 202 and 204, and three or four with at. wt. ranging from 197 to 200. J. H. J. Poole considered the possibility of separating isotopes by centrifuging the liquid at 60,000 rev. per min., when the difference in sp. gr. of the isotopes is 1·5 per 1000, and J. N. Brönsted and G. Hevesy say that a partial separation of the isotopes of mercury was obtained by evaporating mercury at a low press., and condensing the evaporated atoms on a cooled surface—the density of the condensed mercury was 0·999980, and of the residual mercury 1·000031 (mercury unity) when the experimental error was less than one in a million. They also found that when mercury vapour penetrates through narrow openings into a condensation space, the lighter isotope is found in a relatively larger amount than in ordinary mercury. The subject has been also discussed by R. S. Mulliken and W. D. Harkins, W. D. Harkins and S. L. Madorsky, R. S. Mulliken, and W. Jäger and H. von Steinwehr. J. N. Brönsted and G. Hevesy found no measurable difference in the at. wt.

of mercury from different geological and geographical sources, and this makes it probable that the isotopic composition of mercury of terrestrial origin is the same.

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§ 6. Mercurous Oxide

Mercury forms at least two series of compounds in which the mercury behaves as if it were two different elements, for the reactions of the series are quite different. In the mercurous salts the mercury behaves like a univalent element, and in the mercuric salts like a bivalent element. According to H. Kopp,[1] attention was first directed to the lower oxide from the observation that soln. of mercury in nitric acid are different when prepared hot and cold. N. Lemery, for example, showed that the soln. gives different results when treated with salt, and T. Bergman, that the reactions of the two soln. differ in many other respects. It was assumed that more phlogiston was lost when the mercury dissolved in the hot acid than when in the cold acid; and this hypothesis, expressed in terms of Lavoisier's oxidation theory, means that in the one mode of preparation the mercury is in a higher state of oxidation than in the other.

The lower oxide of mercury is called *black oxide of mercury*, and also **mercurous oxide,** Hg_2O. P. Moscati,[2] and G. Moretti obtained it by decomposing a mercurous salt with an aq. soln. of an alkali hydroxide, and washing and drying the product in the dark. M. Donovan treated finely divided mercurous chloride, suspended

in water, with an excess of the alkali; if too little alkali be employed, a basic mercurous chloride is formed, and then oxidized to a basic mercuric chloride, and a further addition of alkali produces a mixture of mercury, mercurous and mercuric oxides. A. Duflos poured a soln. of mercurous nitrate into an alcoholic soln. of potassium hydroxide, and washed and dried the product as before. The product dried over sulphuric acid was found by L. Schaffner to contain no water; but N. J. B. G. Guibourt has stated that it is impossible to obtain pure mercurous oxide because, during the washing, even in the dark, it is resolved into a mixture of mercuric oxide and mercury; J. Lefort also found that the mercurous oxide obtained by precipitation with alkali hydroxide contains mercuric oxide and mercury because it amalgamates gold leaf.

The brownish-black powder has no taste or smell. A sample prepared by C. J. B. Karsten from mercurous chloride and potassium hydroxide had a **specific gravity** 8·9503, and one likewise prepared by W. Herapath, a sp. gr. 10·69—presumably one sample had more free mercury than the other. Analyses were made by N. G. Sefström, M. Donovan, A. F. de Fourcroy and L. J. Thénard, M. Zaboada, N. J. B. G. Guibourt, M. Braamcamp and S. Oliva, etc. The **action of pressure** is to decompose mercurous oxide. F. Streintz found that oxygen is given off when it is compressed between 10,000 and 13,000 atm. The **action of heat** is to decompose mercurous oxide into mercury and mercuric oxide; according to M. Donovan, the reaction takes place at 100°, but A. Vogel obtained no decomposition at this temp. T. Graham, and W. Bruns and O. F. von der Pfordten found the dry powder is decomposed at 100° into mercury and mercuric oxide, and A. F. de Fourcroy and L. J. Thénard, and S. Hada stated that the change occurs slowly at ordinary temp. S. Hada found that mercurous oxide increases in weight when exposed to air. Oxygen is evolved when mercurous oxide is heated to redness. The **action of light** is to resolve mercurous oxide into mercury and mercuric oxide, and, according to G. Suckow, also under a layer of water. M. Berthelot exposed to sunlight some mercurous oxide in an evacuated sealed tube; after a month, some quicksilver had been formed. J. Thomsen gave for the **heat of formation** $(2Hg, O)=42·2$ Cals.; R. Varet, $(2Hg_{liq.}, O)=22·2$ Cals.; and $(HgO_{solid}, Hg_{liq.})=0·7$ Cal. W. Nernst gave $(2Hg, O)=22$ Cals. M. de K. Thompson gave −13,400 cals. for the **free energy** of formation, and −22,200 cals. for the **total energy**. N. R. Campbell found that the **radioactivity** of mercurous oxide is very small. G. A. Dima observed a **photoelectric effect.** J. Gibson found the electrical conductivity increased by exposure to light. F. Streintz noted that the compressed powder at 80° has about one-fourth the **electric resistance** it possesses at ordinary temp. A. J. Allmand noted that the **electromotive force** of mercurous oxide is irregular owing to the tendency to form mercuric oxide.

According to J. W. Fay and A. F. Seeker, mercurous oxide is reduced by **hydrogen** at 80°; but, according to A. Colson, no reduction occurred when heated with hydrogen at 100° for four days, and **oxygen** is rapidly absorbed by mercurous oxide at 100°. C. T. Barfoed, and S. Hada showed that mercurous oxide both oxidizes and dissociates at ordinary temp.; when exposed to air it may increase or decrease in weight according to the conditions—in the closed atm. of moist air it increases in weight, for dissociation is checked and oxidation favoured; but if a large surface is exposed to the open air, it loses in weight, for then dissociation and volatilization of mercury proceed faster than the oxidation of the undecomposed mercuric oxide. M. Rosenfeld showed that when heated in a current of air, the black oxide is produced at 215°, and the red oxide at a higher temp.; the oxidation of mercurous oxide is accelerated if a trace of potassium is present. I. Bhaduri found mercurous oxide to be almost insoluble in cold **water,** but one part of the oxide dissolves in 150,000 parts of warm water. A. von Antropoff observed that **hydrogen peroxide** reacts with explosive violence. The black film which forms on mercury during the pulsating catalytic decomposition of hydrogen peroxide is believed by A. von Antropoff to be *mercurous peroxide* or **mercurous dioxide,** Hg_2O_2, but it decomposes

so easily that it has not been isolated. A. Duflos found the oxide prepared by his process gives up nothing to dil. **hydrochloric acid.** According to J. B. Berthemot, when mercurous oxide is boiled with a soln. of **potassium iodide,** it furnishes mercury and potassium mercuric iodide, while if the mercuric oxide be in excess, mercurous iodide is also formed. J. S. F. Pagenstecher, and L. Thompson found that a conc. soln. of **ammonium chloride** decomposes mercurous oxide with the evolution of ammonia and the formation of mercury and mercuric chloride. According to A. J. Allmand, the **solubility product** $[Hg_2'']$[OH']^2 is $4{\cdot}8\times10^{-24}$. H. Rose found mercurous oxide is decomposed by water, forming mercuric oxide and mercury. K. Brückner found that when triturated dry with **iodine,** and gently heated, mercuric iodide and iodate are formed; the reaction also proceeds slowly in contact with water, or alcohol. J. B. Senderens found that a mixture of **sulphur** and mercurous oxide is inflamed by friction, and sulphur dioxide, mercuric sulphate and sulphide are formed; the reaction with sulphur also occurs under boiling water. According to E. C. Franklin and C. A. Kraus, mercurous oxide is insoluble in liquid **ammonia.** H. Rose found mercurous oxide is decomposed by a soln. of **ammonium nitrate** with the separation of mercury. A mixture of **phosphorus** and mercuric oxide detonates when struck. T. Graham observed that mercurous oxide absorbs that "peculiar principle" which makes **phosphine** spontaneously inflammable, and is slowly decomposed by the gas itself. M. Braamcamp and S. Oliva found **phosphorous acid** reduces mercurous oxide to the metal. C. Reichard found an aq. soln. of **arsenious oxide** has scarcely any action, but the oxide is reduced by alkali or ammonium arsenite. J. W. Fay and A. F. Seeker observed the reduction of mercurous oxide by **carbon monoxide** at 0°. According to G. C. Wittstein, a soln. of **ammonium carbonate** decomposes mercurous oxide into mercuric oxide, which dissolves, and mercury, which remains undissolved. C. R. C. Tichborne found mercurous oxide rubbed with a 10 per cent. soln. of **sodium hydrocarbonate** mixed with phenolphthalein and made colourless by nitric acid does not give a red coloration. A. Fleischer found that mercurous oxide dissolves in a hot soln. of **ammonium thiocyanate,** some mercury separates, and a complex ammonium mercuric thiocyanate is precipitated when aq. ammonia is added to the soln. A. Duflos' preparation dissolved completely in **acetic acid;** H. Erdmann and P. Köthner obtained a white precipitate by treating the acetic acid soln. with **acetylene.** E. G. Burckhardt found the soln. in hot aq. **citric acid,** on cooling, gives a white mixture of mercurous and mercuric salts. J. Peschier stated mercurous oxide is soluble in a soln. of **gum arabic.** J. L. Gay Lussac and L. J. Thénard found that molten **potassium** or **sodium** decomposes mercurous oxide with *une lumière très-vive, et légère détonation.*

G. B. Bird treated a soln. of mercurous nitrate with an alcoholic soln. of potassium hydroxide, all cooled to −42°. A pale amber-coloured precipitate slowly formed which, with rise of temp., changed into the colours of mixtures of mercuric and mercurous oxides and mercury. It was assumed that the pale amber-coloured precipitate was **mercurous hydroxide,** HgOH. C. Reichard also thought that he obtained mercurous hydroxide by digesting mercurous arsenite with an aq. soln. of sodium carbonate. I. Bhaduri said mercurous hydroxide is soluble in hot water and sodium hydroxide; and almost insoluble in cold water.

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§ 7. Mercuric Oxide

In the thirteenth century, the Latin Geber knew that when mercury is heated for a long time, it forms a red calx or oxide; and in his *Summa perfectionis magisterii* he stated that he prepared the calx as a brilliant sublimate by heating a mixture of mercury, nitre, and vitriol. Raymond Lully [1] also prepared the red oxide by calcining the salt obtained by dissolving mercury in nitric acid. The *red oxide of mercury* obtained by these two processes was known to later chemists—*e.g.* A. Libavius—as *mercurius calcinatus per se*, *mercurius præcipitatus per se*, *hydrargyrus calcinatus ruber*, or *mercurius præcipitatus ruber*, etc. The action of heat on mercury and on this oxide was discussed by L. Lemery, R. Boyle, P. Bayen, etc.; and in 1774, there was a controversy between A. Baumé and L. C. Cadet de Gassicourt, as to whether in the absence of reducing agents the red oxide sublimes without decomposition, or is decomposed.

E. Bertrand [2] also found over 22 per cent. of mercuric oxide as an accessory mineral with the hydragryrite of Los Bordos (Chili). Red rhombic needle-like crystals of mercuric oxide were found by A. J. Moses at Terlingua (Brewster County, Texas), and named *montroydite* after Montroyd Sharpe, a mine owner. The crystals occur mixed with mercury and mercuric sulphide. They were studied by W. F. Hillebrand and W. T. Schaller, and B. F. Hill.

The preparation of mercuric oxide.—Mercuric oxide occurs in two forms, yellow and red. Red mercury oxide was prepared by C. E. Weigel [3] by keeping mercury for a month or longer at a boiling heat in a flask filled with air, and having a long loosely fitting tube adapted to its neck. The temp. must not be raised too high, or any oxide which may have been formed will be decomposed—according to W. H. Echols, the temp. of formation is 450°, and the temp. of decomposition 630°, at ordinary press. M. Rosenfeld found that the velocity of oxidation is greatly accelerated if the mercury contains a little potassium. G. B. Taylor and G. A. Hulett heated the mercury 4–7 days to 20° in oxygen under a press. of 2–3 atm. M. E. Chevreul found mercury is covered by a film in freshly prepared oxygen—ozone or chlorine may possibly have been present. H. B. Baker has shown that the vapour of mercury has very little attraction for oxygen. Mercuric oxide is also formed by heating mercury with an oxidizing agent—*e.g.* M. C. Schuyten

used potassium chlorate, and Geber, *vide supra*, nitre. F. L. Winkler reported the presence of some nitre in commercial red oxide of mercury.

F. C. Hoffmann, and J. B. van Mons heated mercurous or mercuric nitrate in a crucible or glass flask on a gradually rising temp. until the nitrous fumes ceased to be evolved. To economize nitric acid, the mercuric nitrate was triturated with an equal weight of mercury before the calcination. E. Kuhn prepared the mercurous nitrate for this purpose by dropping mercury into liquid nitrogen peroxide, and distilling off the excess of the latter. M. Payssé pointed out that if the nitric acid used for making the nitrate contained hydrochloric acid, the resulting oxide will be mixed with some oxychloride. If the nitrate is insufficiently heated —H. C. Vielhaber, C. Jehn, G. Patein—the oxide will contain undecomposed nitrate or some basic nitrate which, according to P. Carles, may be removed by boiling with dil. alkali-lye, or water. P. C. Ray and J. N. Sen calcined mercurous nitrite in a similar manner. G. Brusa and V. Borelli manufactured mercuric oxide by heating mercurous nitrate in a revolving drum connected with a similar revolving drum containing cold mercury. The oxygen and nitrogen peroxide from the hot drum form mercurous nitrate in the cold drum. The mercuric oxide is removed from the first drum, and when it has cooled mercury is introduced. The mercurous nitrate in the second drum is then heated and mercurous nitrate is formed in the first drum, and the operations are repeated again and again. J. Volhard, W. L. Hardin, G. Patein, etc., have given directions for purifying mercuric oxide. J. Myers removed any mercurous oxide in mercuric oxide by heating a mixture of the oxide with ammonium nitrate. The Elektrizitätswerk Lonza obtained mercuric oxide by the electrolysis of alkalies and oxysalts with a mercury anode, and removed the mercury by distillation below say 450°; and the Consortium für Elektrochemie electrolytically oxidized mercury in a soln. of sodium carbonate.

L. V. Brugnatelli showed that mercuric oxide is formed by washing mercuric nitrate many times with boiling water; and N. A. E. Millon, by similarly washing basic mercuric nitrate, or mercuric acetate. The brown oxychloride, $4HgCl_2.HgO$, and the black oxychloride, $HgCl_2.2HgO$, give red oxide when treated with a cold soln. of alkali hydroxide, or a hot soln. of alkali carbonate; many other oxychlorides under similar conditions furnish the yellow oxide. If a soln. of a mercuric salt be treated with an excess of potassium hydroxide, and washed, pale orange-yellow coloured oxide is formed, which, according to M. Siewert, after careful washing still retains one per cent. of mercuric chloride, potassium chloride, and potassium hydroxide. E. P. Schoch gradually added 100 c.c. of a hot soln. of mercuric chloride (1 : 2) to 500 c.c. of a hot soln. of potassium hydroxide (1 : 2), and boiled the mixture 5 hrs. in a flask fitted with a reflux condenser. The product was washed by decantation, and dried on a porous tile. If a cold sat. soln. of a mol of mercuric chloride be added to a cold 2–30 per cent. soln. of at least 10 mols of sodium hydroxide, a pale yellow powder is obtained which, after standing under the mother liquid for some weeks, acquires an orange colour. O. Brunck obtained the yellow oxide by treating a soln. of mercuric nitrate with an excess of sodium carbonate; E. Dufau treated a soln. of mercuric chloride with potassium carbonate; E. Bosetti used barium hydroxide. G. Pinchbeck also gave directions for preparing yellow mercuric oxide.

H. Gaudechon prepared a brown oxide by heating the red oxide to 400°. S. Kern obtained what he regarded as a modification of mercuric oxide by heating the grey precipitate obtained by the action of magnesium on a soln. of mercuric chloride. K. Schick cooled a sat. aq. soln. of mercuric oxide and obtained a white powder, which became yellow when warmed.

C. Paal[4] prepared **colloidal mercuric oxide** by the action of sodium protalbinate or lysalbinate on a soln. of mercuric chloride; Kalle and Co. by the action of the sodium salt of proteic acids on a soln. of a mercuric salt; R. May and co-workers by the action of norgin on an alkaline soln. of mercuric chloride; and E. H. Bunce by the action of potassium hydroxide on an acetone soln. of mercuric chloride.

T. Svedberg obtained colloidal mercuric oxide by the action of an electric discharge on mercuric oxide under isobutyl alcohol. J. Hausmann studied the diffusion of potassium hydroxide in a soln. of mercuric chloride and gelatine.

The characteristics of red and yellow mercuric oxides.—Red mercuric oxide forms scaly shining crystals of a brick-red colour; it also forms a dull flocculent brownish-red crypto-crystalline powder. The colour of the red oxide by grinding becomes orange-yellow, and lighter coloured as the fineness increases. When obtained by precipitation, it forms a light orange-yellow or buff-yellow powder which, after heating, becomes red. J. T. Pelouze [5] thought that yellow mercuric oxide is amorphous, and that red mercuric oxide is crystalline. L. Schaffner, and T. Carnelley and J. Walker believed that the yellow oxide is hydrated, but L. J. Proust, N. A. E. Millon, and W. Wallace showed that it is anhydrous like the red oxide; M. Siewert found a sample dried for 4 days in vacuo at 80° contained 0·5 per cent. of water; E. P. Schoch found a similar amount in a sample air-dried at 115°. According to E. P. Schoch, both the yellow and red oxides are crystalline. He said that the former forms microscopic square tablets, and that if the pale yellow crystals are left in contact with the liquid in which they have been formed, or in a soln. of sodium or potassium chloride, they increase in size, and the colour changes from pale yellow to orange, and in some weeks to a red tint. When the crystals of the yellow oxide are boiled with aq. soln. of salts, they are converted into the prismatic form of the red oxide; the same change takes place when the dry yellow oxide is heated at 250°–600° for 8–24 hrs. The colour of the oxide does not afford trustworthy evidence as to which form is present, since the tabular crystals of the yellow oxide sometimes exhibit a deeper colour than the prismatic crystals of the red variety. On the other hand, A. J. Allmand stated that both the yellow and red modifications occur in prisms and quadratic plates. J. L. Gay Lussac attributed the differences which have been observed in the physical and chemical properties of the two oxides, to a difference in the degree of fineness of the yellow and red oxides. The greater chemical activity of the yellow oxide is a result of the greater surface exposed to the reagent. W. Ostwald, and K. Schick also consider the two modifications to be identical except in the size of the grains.

The following differences in the properties of the red and yellow oxides have been reported. E. P. Schoch found the sp. gr. of the red oxide to be slightly lower than that of the yellow. The errors of experiment in determining the sp. gr. of fine-grained powders are always greater than with coarse-grained homogeneous material. J. T. Pelouze found that when equal quantities of the two oxides are ignited in the same muffle, the yellow oxide volatilizes completely in a time in which the decomposition of the red oxide has scarcely begun. J. L. Gay Lussac and N. A. E. Millon also found that the yellow oxide gives off rather more oxygen than the red in the same time when heated side by side, but the difference is slight. E. P. Schoch stated that the dissociation press. of the yellow oxide at 300°–320° is 760 mm., whereas that of the red does not exceed 400 mm. E. Cohen found a difference of 0·685 millivolt when the two forms of oxide are made into electrodes, Hg | HgO, KOH; but, according to G. Fuseya, this may be an effect of the greater solubility of the more finely divided oxide. According to J. T. Pelouze, dry chlorine acts very slowly on the red oxide at ordinary temp. and not much more quickly when the oxide is powdered, the reaction with the yellow oxide is so vigorous that the mass becomes red hot even when the yellow oxide has been pre-heated to 300°–400°. J. L. Gay Lussac contradicted this in that he found dry chlorine gas produces less hypochlorous anhydride with the red than with the yellow oxide, and he attributed the difference to the smaller surface presented by the red oxide and the formation of a layer of mercuric chloride; the slowness of the reaction with the red oxide results in a slower rise of temp., and consequently this reaction is not so accelerated by temp. as with the yellow oxide. Under water, the two oxides are acted on by chlorine with nearly the same speed, because the mercuric chloride is dissolved as fast as it is formed. N. A. E. Millon found that the red oxide may be boiled with a soln. of oxalic acid without changing very much, while the yellow oxide, even in the cold, is quickly changed to white oxalate. J. Koster and S. J. Stork found that if the red oxide be ground in an agate mortar for 2 hrs. it is as readily acted upon by an aq. soln. of oxalic acid as the yellow oxide. N. A. E. Millon reported also that when boiled with an excess of a soln. of potassium dichromate, the yellow oxide forms the basic chromate, $3HgO.CrO_3$, and the red oxide, $4HgO.CrO_3$. E. Spelta found that when heated in a sealed tube at 150°, the yellow oxide reacts with sulphuryl chloride,

but not so with the red oxide. C. H. Hirzel stated that the yellow oxide, when dried at 40°–50°, reacts with dry ammonia at 100°; but when dried at 160°–180° the oxide is not changed by dry ammonia at 150°. F. Köhler stated that the red oxide is not changed by cold or hot selenium dioxide, or selenic acid, while the yellow oxide forms a basic selenate; and C. F. Rammelsberg made a similar observation with respect to the action of iodic acid. O. Schmieder stated that the red oxide is sparingly soluble in an aq. soln. of ammonium sulphate, and that a white basic salt appears before the liquid is sat.; on the other hand, the yellow oxide readily dissolves in the liquid, and a basic salt separates after the liquid is sat. According to N. A. E. Millon, an alcoholic soln. of mercuric chloride converts the yellow oxide rapidly into oxychloride, $HgCl_2.2HgO$, while the red oxide is scarcely affected. *Vide infra*, chemical reactions.

R. Varet found that the heat of neutralization with hydrocyanic acid is 31·58 Cals. for both the red and yellow oxides; the heat of formation of both oxides is the same, and no heat is evolved when the red oxide passes into the yellow one. The solubility of the yellow oxide in water is greater than that of the red oxide. This is in accord with the general observation that the solubility of a fine-grained powder is greater than that of a coarse-grained powder. G. A. Hulett found that the solubility of ordinary mercuric oxide at 25° is 0·050 grm. per litre, and when finely ground, the solubility rises to 0·150 grm. per litre. When still further comminuted, the solubility of the red oxide can be made to exceed that of the ordinary yellow oxide. R. T. Glazebrook and S. Skinner found that with Gouy's standard cell, the red oxide gives an e.m.f. of 1·384 volts, and the yellow oxide, 1·391 volts. E. Cohen obtained analogous results; but W. Ostwald showed that the differences depend on the different solubilities of the two oxides. Both oxides have approximately the same solubility in *N*-soln. of potassium bromide or iodide, sodium thiosulphate, etc. W. Bersch showed that mercuric oxide reacts with the alkali halides, *e.g.* $HgO+2KCl+H_2O \rightleftharpoons 2KOH+HgCl_2$, until equilibrium is reached. The cell $Hg \mid HgO_{yellow} \mid KOH_{soln.} \mid HgO_{red} \mid Hg$, in consequence, gives an e.m.f. of 0·001 volt which is well within the range of experimental error.

The physical properties of mercuric oxide.—F. A. C. Gren [6] said that mercuric oxide has a disagreeable metallic taste; and it is a violent acrid poison. The **colour** has been previously discussed. F. A. C. Gren, E. J. Houston, and G. F. Hildebrandt showed that when the red oxide is heated, it darkens in colour and becomes violet-black, but the original red colour is restored on cooling (*vide* **2.** 18, 13). E. P. Schoch also found that when the yellow oxide is heated under water, it becomes red, and the original yellow colour is restored on cooling. B. Schwalbe found that when the red oxide is cooled to —86°, it is nearly colourless. According to M. Saladin, obtuse rhombohedral **crystals** were formed in a bottle containing the pharmaceutical preparation *aqua phagadœnica*—a mixture of lime-water and mercurous chloride. W. F. Hillebrand and W. T. Schaller found that the crystals of montroydite are holohedral and rhombic with the axial ratios $a:b:c = 0{\cdot}6375:1:1{\cdot}1977$. A. des Cloizeaux stated that the tabular crystals obtained by heating mercury for a long time in air are monoclinic prisms with axial ratios $a:b:c = 0{\cdot}6728:1:0{\cdot}3185$, and $\beta = 117°\ 29'$; P. Groth recalculated the data and obtained $a:b:c = 0{\cdot}5979:1:0{\cdot}6367$, and $\beta = 90°\ 56'$. O. G. Nordenskjöld obtained $a:b:c = 1{\cdot}5330:1:1{\cdot}4500$, and β approximately 90°, or, recalculated by P. Groth, $a:b:c = 1{\cdot}1498:1:1{\cdot}875$, and β approximately 90°. For E. P. Schoch's and A. J. Allmand's observations, *vide supra*.

A. le Royer and J. B. A. Dumas gave 11·29 for the **specific gravity** of mercuric oxide in vacuo; W. Herapath, 11·074–11·085 (17·5°–18·3°); P. F. G. Boullay, 11·0; C. J. B. Karsten, 11·1909 (4°); L. Playfair and J. P. Joule, 11·136–11·344 at 3·9°; and E. P. Schoch, at 27·5°, gave 11·03 for the yellow oxide, 11·08 for the red oxide, and for the red oxide finely ground, 11·21. W. F. Hillebrand and W. T. Schaller gave between 2 and 3 for the **hardness** of montroydite; and A. J. Moses gave less than 2. W. Spring studied the **effect of pressure** on mercuric oxide, and M. C. Lea reported that this oxide darkens slightly but very distinctly under press., and this change seems to be accompanied by a slight loss of weight, requiring, however, very careful weighing to detect it. The darkened part, as well

as the rest, dissolves without difficulty in acetic acid, and consisted, therefore, probably of traces of mercurous oxide and not of metallic mercury.

According to C. Zenghelis, mercuric oxide is volatile at ordinary temp., and a gold plate a short distance away is attacked, a silver plate more so. A. J. Allmand gave 6×10^{-22} atm. at 18° for the **dissociation pressure** of mercuric oxide; V. Rothmund gave $10^{-10\cdot96}$ atm., or $10^{-8\cdot08}$ mm. at room temp. G. B. Taylor and G. A. Hulett gave for the dissociation press., p, at $T°$ K., $\log p=-5273\cdot5T^{-1}+1\cdot75\log T-0\cdot001033T+5\cdot9461$—*vide* **1.** 8, 2. J. Kendall and F. J. Fuchs found that the oxides of copper, manganese, iron, cerium, silicon, and chromium accelerated the thermal decomposition of mercuric oxide. J. Joubert found the oxide to be perceptibly decomposed at 100°. The **action of heat** is such that, according to W. H. Echols, decomposition begins at 630°, and combination at 450°. At a red heat, therefore, mercuric oxide volatilizes completely, for it is resolved into oxygen and mercury vapour, and if heated in a distilling apparatus, the mercury vapour takes up some oxygen on cooling, and this collects on the surface of the mercury in the receiver. E. P. Schoch found the dissociation press. of the yellow oxide is greater than that of the red oxide at about 300°—*vide supra.* The equilibrium conditions in the heterogeneous system $2HgO\rightleftharpoons2Hg+O_2$ have been studied by J. Myers, H. Pélabon, H. Debray, H. W. B. Roozeboom, and G. B. Taylor and G. A. Hulett—*vide* **1.** 8, 2. O. Brunck found that 2·5 to 4 per cent. of the oxygen is ozonized, but not if the oxide is heated in air; with a mixture of potassium chlorate and mercuric oxide, no ozone is formed. A. R. Leeds thought that the supposed ozone formed by heating mercuric oxide is really chlorine present as an impurity in the oxide. According to M. Goldstein, the **molecular heat** is 5·6. H. Kopp gave 0·0530 for the **specific heat** between 15° and 52°; H. V. Regnault, 0·0518 between 5° and 98°; and A. S. Russell, 0·0355 between —190° and —80°; 0·0449 between —74° and 0°; and 0·0503 between 3° and 43°. The **heat of formation** or decomposition, according to M. Berthelot, is 21·5 Cals.—the same for red or yellow oxide, as subsequently found by R. Varet—*vide supra.* J. Thomsen gave (Hg, O)=30·67 Cals.; W. Nernst, 20·7 Cals.; R. Varet, 21·5 Cals.; and G. B. Taylor and G. A. Hulett, 21·4 Cals.

E. L. Nichols and B. W. Snow measured the **reflecting power** for light of different wave-length at 25°, 313°, and 523°. Mercuric oxide gradually blackens when exposed to sunlight, being superficially decomposed into mercury and oxygen, according to N. J. B. G. Guibourt, or into mercury and mercurous oxide, according to M. Donovan. No evolution of gas was observed by G. Lemoine during the decomposition of mercuric oxide in sunlight. M. Berthelot found that red mercuric oxide is more rapidly decomposed by sunlight than the yellow oxide; this is partly due to the colour and to the texture of the powder; the action is much increased if moisture be present. G. A. Dima studied the **photoelectric effect** of mercury oxide; and N. R. Campbell, the **radioactivity.**

K. Schick found the sp. **electrical conductivity** of aq. soln. to be $2\cdot1\times10^{-6}$ at 25°. A. J. Allmand has measured the **difference of potential** with red and yellow mercuric oxide, and N- and $\frac{1}{10}N$-soln. of potassium or sodium hydroxide. M. Chow measured the e.m.f. of hydrogen and mercuric oxide cells, and of mercuric oxide and amalgam cells. A. Iljeff measured the **thermoelectric force** of two pencils of compressed mercuric oxide. J. Habermann, and P. Bunge, showed that a mercury cathode with a 1 cm. layer of mercuric oxide does not give off hydrogen in the electrolysis of organic liquids. P. T. Muller and H. Allemandet, and A. Heil considered the use of mercuric oxide as a **depolarizer** in galvanic elements.

The chemical properties of mercuric oxide.—Mercuric oxide is readily reduced by **hydrogen.** S. Hauser[7] found the temp. of the reduction of the yellow oxide to be 64°–76°; and of the red oxide, 164°–195°. According to A. Colson, the yellow oxide reduced about five times as rapidly as the red oxide; the rapidity of attack is not proportional to the press. but more nearly to the cube root of the press. W. Müller-Erzbach observed no reduction by hydrogen at 200°, a slight action at 220°, and more at 230°; and with the yellow oxide the action begins at 127°. I. W. Fay

and A. F. Seeker detected a reduction with the yellow oxide at 50°, and with the red oxide at 115°; F. Glaser's numbers are respectively 75° and 91° for the yellow and red precipitated oxide, and 140° for the red oxide prepared by heating mercury in oxygen. F. G. Donnan and A. J. Allmand compute the thermal value $H_2+HgO=Hg+H_2O+46{\cdot}75$ Cals. from measurements of the e.m.f. A. von Antropoff found that the red oxide suspended in water is not changed by the passage of **ozonized oxygen** for three days. M. Traube found mercuric oxide is oxidized by **hydrogen peroxide**; and M. Martinon, that it is reduced by hydrogen peroxide in alkaline soln.

According to A. L. Lavoisier and C. M. Cornette [8] precipitated yellow mercuric oxide is soluble in **water,** but not the red oxide. L. Thompson and N. J. B. G. Guibourt also noted the solubility of mercuric oxide in water. E. F. Anthon found the oxide to be sparingly soluble in cold, and more soluble in hot water. The statement, however, was contested by the early workers, and some believed that the alleged solubility was a mal-observation due to the use of an oxide contaminated with the nitrate; but R. F. Marchand, F. H. Boudet, and A. Gossmann showed that the oxide free from nitrate is dissolved by water. A. Bineau found that a litre of water dissolves 0·033 grm. of yellow or red mercuric oxide; and W. Wallace, that a litre of water dissolves 0·005 grm. of yellow oxide after standing for a long time in contact with one another, and 0·008 grm. after boiling and cooling. G. A. Hulett found a litre of water at 25° dissolves 0·05 grm. of coarse-grained red oxide, and 0·15 grm. of the fine-grained red oxide. K. Schick gave for the solubility of the yellow oxide in a litre of soln., 0·0518 grm. at 25°, and 0·410 grm. at 100°; and the red oxide, 0·0513 grm. at 25°, and 0·379 grm. at 100°—longer contact would probably have given better agreement between the results with the red and yellow oxides. He estimated 2 per cent. **ionization** occurs in aq. soln. A. J. Allmand gave for the **solubility product,** 4×10^{-26} at 18°; H. Grossmann gave the same value; and S. Labendzinsky, $1{\cdot}5\times10^{-26}$.

According to H. Moissan,[9] **fluorine** attacks mercuric oxide with the development of heat. M. Braamcamp and S. Oliva found that at a red heat, **chlorine** decomposes mercuric oxide into oxygen and mercuric chloride, but at lower temp., chlorine monoxide and mercuric chloride or oxychloride are formed; and with mercuric oxide suspended in boiling water, chlorine forms mercuric chloride and chlorate. A. Michael and A. Murphy found that a 10 per cent. soln. of chlorine scarcely attacks mercuric oxide under conditions where the gas readily attacks the oxide. According to E. Lippmann, a soln. of **iodine** in water, alcohol, benzene, acetone, or carbon tetrachloride—but not in alcoholic phenol—when boiled with mercuric oxide in a reflux condenser forms mercuric iodide, and an oxyiodide—possibly the iodate: $6HgO+6I_2=5HgI_2+Hg(IO_3)_2$. K. Brückner noted the formation of mercuric iodide and iodate in aq. soln., but in alcoholic soln. some aldehyde was formed. R. L. Taylor noted that freshly precipitated mercuric oxide gives mercuric hypoiodite when treated with iodine dissolved or suspended in water. A. Jäger found the solubility of mercuric oxide in aq. **hydrofluoric acid** of normality N, to be:

N	0·12	0·24	0·57	1·11	2·17
Mol per litre	0·01258	0·0247	0·0629	0·1168	0·2586

If alkali fluorides be also present the solubility is reduced; H. Pick gave $1{\cdot}8\times10^{-25}$ for the solubility product. O. D. Sweet found that **hydrochloric acid** mixed with ammonium chloride is a good solvent for mercuric oxide. S. M. Tanatar and L. Pissarjewsky found the heat of soln. in 0·1N-alcoholic soln. hydrochloric acid to be 18·9 Cals., and M. Berthelot gave 9·45 Cals. for the heat of neutralization of $\frac{1}{2}HgO$ with hydrochloric acid (one eq. per litre). According to E. P. Schoch, the water solubility of mercuric oxide is raised in the presence of **alkali chlorides;** C. Jehn, and H. Grossmann found the oxide to be readily soluble in a soln. of **potassium iodide,** forming, according to E. Rupp and W. F. Schirmer, potassium hydroxide and potassium mercuric iodide, K_2HgI_4. G. André, found mercuric

oxide to be soluble in conc. soln. of the **alkaline earth chlorides** and of **magnesium chloride.** W. Bersch found that the **alkali halides** are decomposed by mercuric oxide, forming the mercuric halide and the alkali hydroxide until equilibrium is attained, but if an insoluble mercuric halide is formed, and an excess of mercuric oxide be present, all the halogen is abstracted from the soln. The state of equilibrium is dependent on the heat of reaction; if heat is absorbed, the quantity of free alkali increases with rise of temp. and *vice versâ*. The time required to reach the final state of equilibrium is dependent on the halogen—it is smallest with the iodides, and decreases as the temp. is raised. The amount of decomposition depends mainly on the halogen, the alkali metal has very little influence on the result. O. Kühling, M. Dranty, and E. Dufau studied the action of soln. of **sodium chloride.** According to W. R. Hodgkinson and F. K. Lowndes, when mercuric oxide is added to molten **potassium chlorate,** there is an increase in the speed of evolution of oxygen, and chlorine is formed. O. Brunck also studied this reaction, *vide supra.*

When mercuric oxide is heated with **sulphur** in a retort, L. J. Proust[10] observed a violent explosion; and J. B. Senderens found that by rubbing together sulphur, mercuric oxide, and a little water, and heating the mixture to 100°, mercuric sulphide and sulphate were formed. F. C. Phillips found that mercuric oxide suspended in water is slowly turned grey and then blackened by **methyl hydrosulphide.** R. W. Bunsen used mercuric oxide for oxidizing metal sulphides into oxides, F. W. Schmidt said that basic sulphates may be formed. According to D. L. Hammick, **sulphur dioxide** is oxidized by heated mercuric oxide forming mercury, sulphur trioxide, and mercurous and mercuric sulphates. A. Vogel found that mercuric oxide is reduced by **sulphurous acid** to sulphuric acid and mercury; but if the proportion of sulphurous acid be small, there is a rise of temp. and some mercurous sulphate, Hg_2SO_4, is formed, and in part dissolved; that in soln. is very slowly reduced by the sulphurous acid to mercury. The precipitation is complete if sufficient acid be present. G. Oddo and U. Giachery represented the quantitative reaction with **sulphur monochloride:** $2HgO+2S_2Cl_2=2HgCl_2+SO_2+3S$. E. Spelta noted that **sulphuryl chloride,** SO_2Cl_2, does not react with cold or hot mercuric oxide prepared in the dry way; but with the yellow oxide, mercuric sulphate and chloride are formed. H. B. North found sulphuryl chloride reacts slowly at ordinary temp. and press. with the yellow oxide and a mixture of mercurous and mercuric chlorides was formed in a few days. The yellow oxide acts more vigorously than the red oxide when heated with sulphuryl chloride in a sealed tube—some sulphur trioxide is formed. The yellow oxide reacts vigorously with **thionyl chloride,** $SOCl_2$, and a white mixture of mercurous and mercuric chlorides is formed; with a large proportion of thionyl chloride: $HgO+5SOCl_2=HgCl_2+3SO_2Cl_2+S_2Cl_2$; and with a small proportion: $HgO+SOCl_2=HgCl_2+SO_2$. K. Barth noted that a complex is formed when mercuric oxide is treated with **sodium hydrosulphate:** $HgO+2NaHSO_4=Hg(NaSO_4)_2+H_2O$. W. Spring found mercuric oxide reacts with sodium hydrosulphate under the influence of great press. J. Landauer and F. J. Faktor found mercuric oxide is blackened by **sodium thiosulphate,** and mercuric sulphide is formed. A. Seyewetz and P. Trawitz found that the oxide dissolves in a hot soln. of **ammonium persulphate,** giving off oxygen and forming a sulphate.

According to J. Kjeldahl,[11] and C. Arnold and K. Wedemeyer, mercuric oxide at 400° acts as an oxidizing agent for **nitrogen,** and can be utilized in organic analytical work. G. Gore and E. C. Franklin and C. A. Kraus found both yellow and red mercuric oxides are insoluble in liquid **ammonia.** A. L. Lavoisier referred to the solubility of mercuric oxide in aq. ammonia; and he added that on evaporation the soln. furnishes a white salt in which the mercuric oxide *fait alors l'office d'acide.* L. Cramer obtained what he regarded as *mercuric dotrita-ammino-oxide,* $3HgO.2NH_3$, by mixing an emulsion of gum arabic and mercuric oxide with ammonia. It is stated to blacken on exposure to light. S. Hauser studied the reduction of mercuric oxide by ammonia gas. A. Guyard found the oxide is soluble in ammoniacal soln.

of **ammonium salts.** F. Ephraim found **sodamide** is reduced and sodium amalgam is formed. According to P. Sabatier and J. B. Senderens, **nitric oxide** is not changed by mercuric oxide at 300°, but at 400°, nitrous fumes are formed and the oxide dissociates. According to W. Lossen, and A. Thum, **hydroxylamine** rapidly reduces mercuric oxide to the metal; the reaction has been studied by W. Zorn, E. Divers, W. F. C. Dresler and R. Stein, and M. Adams. The latter found the oxide is dissolved at 0° by an alcoholic soln. of hydroxylamine hydrobromide. Mercuric oxide is vigorously reduced by **hydrazine** hydrate, and the reaction has been studied by T. Curtius and R. Jay, F. Schrader, L. de Bruyn, A. W. Browne and F. F. Shetterly, etc. C. F. Hale and V. E. Nunez represented the reaction: $N_2H_4.H_2O+2HgO=N_2+2Hg+3H_2O$. O. D. Sweet found **nitric acid** to be a good solvent for mercuric oxide. E. Divers found the **hyponitrites** are oxidized by mercuric oxide to nitrites.

A mixture of mercuric oxide and **phosphorus** detonates when struck with a hammer; and when boiled with water and phosphorus. B. Pelletier [12] noted that mercury phosphide and phosphoric acid are formed; at ordinary temp. M. Braamcamp and S. Oliva, and A. Granger found that mercury is produced, but they say that no phosphoric or phosphorous acid appears to dissolve in the water—possibly a phosphate is formed; they also stated that **phosphorous acid** reduces mercuric oxide to mercury, and phosphoric acid is formed. B. E. Howard also found **hypophosphorous acid** reduces mercuric oxide explosively to the metal. K. Haack found mercuric oxide to be insoluble in **phosphoric acid, arsenic acid,** and in soln. of the primary and secondary **alkali phosphates** and **alkali arsenates.** C. Reichard studied the action of red and yellow mercuric oxides on soln. of arsenious oxide in sodium hydroxide, and when the soln. is warmed, the mercury is reduced. A. Vogel found powdered **antimony** reduces mercuric oxide when the mixture is heated.

According to A. Gautier,[13] **carbon monoxide** does not act on moist mercuric oxide; but I. W. Fay and A. F. Seeker found that the yellow oxide is reduced in 6 hrs. at 0°, and the red oxide likewise at 95°. L. Moser and O. Schmid said that the yellow oxide is quantitatively reduced at 100°, but not the red oxide. S. Hauser gave 95° for the temp. of the reaction with red oxide, and 50° with the yellow oxide. F. von Kügelgen reduced mercuric oxide by heating it with **calcium carbide.** C. R. C. Tichborne found that a red coloration appears when mercuric oxide is triturated with a 10 per cent. soln. of **sodium hydrocarbonate** mixed with phenolphthaleïn, and just decolorized with nitric acid. L. N. Vauquelin found that the action of mercuric oxide on **cyanogen** resembles that of the alkali hydroxides—the undissolved oxide turns brown, and mercuric cyanide and ammonium carbonate are formed. M. Berthelot gave for the heat of the reaction at 15° between mercuric oxide and **hydrocyanic acid** (1 eq. per litre), 31 Cals. for the solid salt, and 34 Cals. for the salt in soln. G. McP. Smith found red mercuric oxide reacts in the cold with a soln. of potassium ferricyanide, forming ferric hydroxide, potassium hydroxide, and mercuric cyanide; with an excess of the ferricyanide, mercuric oxide dissolves, ferric hydroxide is deposited, and the soln. deposits crystals of mercuric cyanide. F. Selmi found that when **ferric potassium ferrocyanide**—soluble prussian blue—is boiled with water and mercuric oxide, mercuric cyanide is formed; **silver ferrocyanide** was found by W. Weith to have very little action; **potassium cobalticyanide** to have none at all; F. Sönderop found that a boiling soln. of potassium cobalticyanide form potassium hydroxide and cobaltous mercuricyanide, $CO_2Hg_3Cy_{12}$; E. Lehmann, that **potassium manganicyanide,** K_3MnCy_6, forms mercuric cyanide and manganese sesquioxide; C. Rölcke, that **potassium chromicyanide,** K_3CrCy_6, forms chromium hydroxide, mercuric cyanide, and chromous mercuricyanide, $Cr_2Hg_3Cy_{12}$; the Badische Anilin- und Sodafabrik patented the formation of ammonia by the action of mercuric oxide on **titanium cyanonitride.** A. Fleischer found mercuric oxide is copiously dissolved by cold or hot soln. of **ammonium thiocyanate.**

Mercuric oxide acts as an oxidizing agent on many organic compounds and is thereby reduced to mercurous oxide or the metal—*e.g.* A. Vogel found soln. of **sugar**

or **lactose** reduced mercuric to mercurous oxide, and in the presence of potassium hydroxide, A. C. Becquerel found the metal is produced. According to P. Sabatier and A. Mailhe, **alcohol** at 150°–250° forms carbon dioxide and acetaldehyde—not acetic acid; and, according to F. Bullnheimer, **glycerol** reduces the oxide to the metal. A. Connell found that mercuric oxide dissolves in a boiling mixture of acetic and formic acids, and P. A. von Bonsdorff found that this oxide is not decomposed with a soln. of potassium chloride and **sodium formate,** but when heated with potassium chloride and free **formic acid,** carbon dioxide is evolved, and some potassium formate, mercuric chloride, and mercury are produced. K. Brand studied the solvent action of **trichloroacetic acid;** W. Traube and B. Löwe, that of **ethylenediamine;** K. A. Hofmann, of **acetone, propyl alcohol, benzene, chloroform, petroleum,** etc.; H. Wilfarth showed that the presence of mercuric oxide accelerates the oxidation of organic substances by sulphuric acid; and A. Halenke used it for oxidizing organic matters. H. Erdmann and H. Köthner found that mercuric oxide favoured the continuous formation of acetaldehyde by passing acetylene into a boiling mixture of sulphuric acid and water. Mercuric oxide is soluble in picric acid (R. Varet); alkali phenoldisulphonate (A. and L. Lumière and M. Chevrotier); formamide (B. Fischer and B. Grützner); benzamide (V. Dessaignes); soln. of gum arabic (J. Peschier); etc. Mercuric oxide forms complexes with many organic compounds. According to S. M. Auld and A. Hantzsch, freshly precipitated mercuric oxide does not dissolve in acetone, but it readily dissolves if a trace of alkali hydroxide is present; it behaves similarly with **acetaldehyde;** and it does not dissolve in **acetophenone** unless the mixture is warmed to 100°.

E. Lay [14] found mercuric oxide decomposed heated silicon hydrogen-nitrogen compounds—*e.g.* Si_2N_3H; O. Ruff and K. Albert reduced **silicochloroform,** $SiHCl_3$; and G. Rauter reduced **silicon tetrachloride,** $SiCl_4$, between 250° and 260°. C. Chabrié and F. Levallois found **ultramarine** is desulphurized by treatment with silver chloride. J. L. Gay Lussac and L. J. Thénard [15] found that mercuric oxide is reduced by molten **potassium** or **sodium** in a similar manner to mercurous oxide. N. N. Beketoff obtained a mixture of Na_2Hg and Na_2HgO_2 by heating eq. quantities of sodium and mercuric oxide. C. Winkler reduced the oxide by heating it with **magnesium;** A. Vogel, by heating it with **zinc** or **tin** filings; and A. Stavenhagen and E. Schuchard, by warming it with **aluminium.**

E. P. Schoch [16] stated that mercuric oxide is not much more soluble in an aq. soln. of **sodium hydroxide** than it is in water, but K. Schick stated that its solubility in $\frac{1}{50}N$-KOH is 25 per cent. greater than in water. G. Fuseya found the solubility of mercuric oxide at 25°, when K denotes the equilibrium constant, to be:

NaOH	0	0·0096	0·0955	0·502	1·0758	2·09 mols per litre.
HgO	23·4	24·6	24·9	26·6	28·3	30·9 millimols per litre.
K	—	—	0·0047	0·0049	0·0050	0·0051

The sudden change in the solubility of the oxide in passing from neutral to alkaline soln. is thought to be due to the greater dispersion of the mercuric oxide in alkaline soln. Assuming that the steady increase in the solubility of mercuric oxide as the conc. of the sodium hydroxide increases, is due to the hydrated mercuric oxide acting as a weak acid, **mercuric acid,** H_2HgO_2, and since the increase in solubility is proportional to the first power of the conc. of the OH′-ion, G. Fuseya represents the reaction $Na^{\cdot}+OH'+HgO_{solid}=Na^{\cdot}+HHgO_2'$, and calculates the equilibrium constant K, from $K=[HHgO_2']/OH']$. He estimated the ionization constant of the first hydrogen of mercuric acid to be $1{\cdot}7\times10^{-15}$. J. Hausmann studied the diffusion of mercuric chloride in gelatine containing **potassium hydroxide** in soln. S. Meunier showed that a little mercuric oxide readily dissolves in molten potassium hydroxide over 400° without the evolution of gas, forming a colourless liquid. The cold cake when slowly cooled is brownish-violet, and when extracted with water furnishes some amorphous mercuric oxide and rhombic octahedra of **potassium mercuriate,** $K_2Hg_2O_3$—sp. gr. 10·31. When the crystals are heated, the mercuric

oxide volatilizes from the crystals, and leaves behind potash. They are gradually decomposed by water, and more slowly still by alcohol. S. Meunier obtained similar crystals of what he regarded as **sodium mercuriate,** $Na_2Hg_2O_3$, in an analogous manner. K. Schick obtained what was assumed to be **barium mercuriate,** $BaHg_2O_3.H_2O$, by mixing a 0·26*N*-soln. of barium hydroxide with levigated yellow mercuric oxide. C. L. Berthollet boiled mercuric oxide with lime-water, and on evaporation obtained yellow crystals thought to be **calcium mercuriate.**

B. Finzi said that mercuric oxide dissolves in soln. of **silver sulphate, nitrate,** or **acetate.** V. Kohlschütter and A. d'Almendra found that if mercuric oxide be immersed in a soln. of silver nitrate containing some free acetic acid, a deposit of metallic silver is formed on the oxide—*vide* zinc oxide. A. Mailhe precipitated basic salts by adding mercuric oxide to soln. of **cupric chloride, bromide, or nitrate,** while **cupric sulphate** is but slowly and incompletely attacked. Basic salts were also obtained by A. Mailhe, and G. André from soln. of **zinc chloride, bromide, or nitrate ;** the former found no precipitation occurs with **cadmium sulphate,** but basic salts were obtained with **cadmium chloride, bromide, or nitrate.** L. Barthe found mercuric oxide to be sparingly soluble in a cold soln. of **mercuric cyanide,** but copiously at 75° with the evolution of hydrocyanic acid. A. Vogel noted that an aq. soln. of **stannous chloride** gives a precipitate of the metal and a basic salt—stannic chloride is formed. A. Mailhe obtained a precipitation of basic chloride from soln. of **lead chloride,** but no visible change with **lead nitrate** soln. Basic bismuth chloride is precipitated when mercuric oxide is dissolved in a cold soln. of **bismuth trichloride ;** a basic bismuth nitrate also precipitates from soln. in **bismuth nitrate.** E. F. Smith and P. Heyl found that chromium, iron, and aluminium are completely precipitated as hydroxides or basic salts from soln. of their salts by the addition of mercuric oxide, while zinc, cobalt, nickel, uranium, beryllium, cerium, and lanthanum are partially precipitated from cold soln., and more completely from hot soln. B. Finzi also examined the action of soln. of salts of chromium, aluminium, manganese, iron, nickel, and cobalt on mercuric oxide. C. Zimmermann found that mercuric oxide does not precipitate uranyl hydroxide from soln. of **uranyl nitrate,** but it does so quantitatively from **uranyl chloride** soln. or mixtures of the nitrate with alkali chloride ; and G. Alibegoff used the reaction for the separation of uranium from the alkalies and alkaline earths. A. Mailhe found that mercuric oxide is soluble in soln. of uranium nitrate and **aluminium nitrate** and a basic mercuric nitrate is formed ; and also that freshly precipitated mercuric oxide added to soln. of **manganous chloride** causes the separation of manganese hydroxide which rapidly forms a higher oxide and an oxychloride ; no visible change occurs with soln. of **manganous sulphate ;** and a mangano-mercuric nitrate is obtained in soln. of the nitrate. J. Volhard, and C. Meineke precipitated manganese dioxide, MnO_2, by treating a soln. of **manganese sulphate or nitrate** with mercuric oxide and bromine water. According to A. Duflos, mercuric oxide is reduced to mercurous oxide by **ferrous hydroxide** or **ferrous salts ;** A. Mailhe obtained a precipitation of a basic ferric chloride from soln. of **ferrous chloride ;** a basic sulphate from soln. of **ferrous sulphate ;** a basic mercuric salt from soln. of **ferric chloride, ferric sulphate,** or **ferric nitrate.** He also obtained a precipitation of basic salts from soln. of **nickel chloride or nitrate ;** and from soln. of **cobalt chloride or nitrate.** C. Zimmermann utilized the reaction for separating cobalt and nickel from iron and aluminium chlorides or sulphates.

Mercuric hydroxide.—The aq. soln. of mercuric oxide, according to N. J. B. G. Guibourt,[17] and M. Donovan has a metallic taste, and when exposed to the air, becomes covered with a film of mercury ; it is coloured brown by hydrogen sulphide ; and gives a white turbidity when slightly diluted with ammonia ; and it also colours the juice of violets green. J. Fonberg found that the soln. does not act on turmeric ; and F. H. Boudet, that it colours litmus blue ; A. Bineau also stated that it acts on litmus after admixture with a salt soln. N. Pappada found colloidal mercuric oxide to be soluble in a soln. of mercuric oxide. T. Carnelley

and J. Walker claimed to have made mercuric hydroxide, $Hg(OH)_2$, by adding sodium hydroxide to a soln. of mercuric chloride, and drying the precipitate in air; only about $\frac{1}{2}$ per cent. of water is lost at 100°, and all—about 8·5 per cent.—is lost at 175°; at higher temp. oxygen begins to be evolved. The ionic solubility found by W. Biltz and F. Zimmermann is about 10^{-9}; and H. Ley and H. Kissel said that the basicity of mercuric hydroxide is very small, and approaches that of aniline. M. Kolthoff saw that the ionization of mercuric hydroxide involves the consecutive reactions $Hg(OH)_2 \rightleftharpoons HgOH^{\cdot} + OH' \rightleftharpoons Hg^{\cdot\cdot} + 2OH'$. When mercuric hydroxide is boiled with an ammonium salt soln., H. Grossmann found that complex salts are formed. N. G. Chatterji and N. R. Dhar said that mercuric hydroxide is peptized by soln. of sodium hydroxide in the presence of glycerol or sugar because the electrical conductivity of the alkali soln. is not appreciably changed by the mercuric hydroxide.

Mercuric dioxide or peroxide.—According to A. von Antropoff,[18] mercurous oxide reacts with hydrogen peroxide with explosive violence even in the presence of free acid; after repeated additions of peroxide, the reaction ceases, and the black oxide assumes a dark red colour, due to the formation of mercuric peroxydate. Mercuric dioxide seems to be formed in the catalytic decomposition of hydrogen peroxide; and by the interaction of an alcoholic soln. of mercuric chloride with hydrogen peroxide in the presence of the theoretical amount of potassium hydroxide in alcoholic soln. G. Pellini prepared this compound in a similar manner. Some specimens of red oxide immediately decompose the hydrogen peroxide with evolution of oxygen, but the addition of a minute quantity of nitric acid will prevent this and induce the formation of the peroxydate. The compound cannot be obtained by the action of hydrogen peroxide on mercuric acetate, or by the action of ozone on mercury or mercuric oxide. Analyses of the red compound show that it has the composition HgO_2, and it can be regarded as the mercuric salt of hydrogen peroxide, that is, *mercuric peroxydate*, Hg(O.O). It decomposes rapidly when in contact with water at the ordinary temp. with evolution of oxygen. It is slowly hydrolyzed by water at 0°; the washings contain free hydrogen peroxide, and mercuric oxide is formed ultimately. The dark red compound is not formed when the red oxide is left in contact with hydrogen peroxide of 15 per cent. or less conc., although even in these cases evolution of oxygen occurs after some little time. The peroxydate is formed more readily at the ordinary temp. than at 0°, but this is followed by vigorous decomposition in the course of twenty to fifty minutes, whereas at 0° decomposition occurs after three to seven days. The decomposition is accelerated by traces of alkali, but retarded by acids. Yellow mercuric oxide cannot be used in place of the red oxide, but, if the red oxide is powdered until it has a yellow colour, it reacts readily with hydrogen peroxide; the product formed has a paler colour, and decomposes much more readily than the product from the ordinary red oxide. When dry, the compound is comparatively stable, even at ordinary temp. It can undergo rapid decomposition, leaving a grey residue; this usually occurs at the beginning of drying; or it can decompose slowly, giving up oxygen and leaving a residue of red mercuric oxide. When heated or struck, it explodes, and the product obtained from the finely powdered oxide explodes when rubbed, even in the moist state. Daylight has no apparent effect on the decomposition of the dry powder. Acids decompose mercuric dioxide, forming mercuric salts and hydrogen peroxide; with hydrochloric acid chlorine is evolved; with potassium iodide, iodine is formed; and a soln. of potassium permanganate is decolorized. The feeble basic character of mercury corresponds with the relative instability of the compound when compared with the corresponding dioxides of magnesium, zinc, and cadmium.

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§ 8. Mercury Ammonium Compounds

Neither **mercuric-amide,** $Hg(NH_2)_2$, nor **mercuric-imide,** HgNH, has been prepared, although a derivative of phenylamine, $C_6H_5NH_2$, namely, **mercuric phenyl-amide,** $Hg(NHC_6H_5)_2$, has been obtained. Reactions which might have been expected *a priori* to give these compounds—*e.g.* treatment of potassamide in liquid ammonia with a mercuric salt—give the end-product, **mercuric nitride,** Hg_3N_2; thus, with mercuric iodide: $3HgI_2+6KNH_2 \rightarrow Hg_3N_2+6KI+4NH_3$.

Mercurous ammonia compounds.—Numerous ammonia derivatives of mercuric salts are known, but not of mercurous salts. Hydrazine, which resembles ammonia in some respects, is reported to form with mercurous nitrate, a white crystalline addition compound, **mercurous hydrazine nitrate,** $N_2H_4.2HgNO_3$; but the corresponding ammonia compound has not yet been obtained. It seems as if mercurous compounds break down into mercury and mercuric salts as soon as the attempt is made to prepare ammonia derivatives. This is supposed to be explained by assuming that the mercurous chloride is slightly dissociated: $2HgCl \rightleftharpoons Hg+HgCl_2$, and the equilibrium is slightly disturbed by the addition of ammonia, for the ammonia reacts with the mercuric chloride, forming an insoluble amide; this

reduces the conc. of the mercuric salt, and accordingly more is formed to restore equilibrium, and as this action continues the dissociation proceeds to an end. This corresponds with the fact that nearly all the mercurous ammonia compounds which have been reported are black—presumably owing to the presence of free mercury in a finely divided state. J. G. F. Druce [1] said that hydrochloric acid is first produced in the reaction and then neutralized. According to the routine process employed in qualitative analysis, when separating a mixture of mercurous and silver chlorides, the mercurous chloride is turned black on the addition of aq. ammonia; the black substance was formerly considered to be *dimercuroammonium chloride*; later, the black precipitate was thought to be a *dimercuric amidochloride* formed by the reaction:

$$\begin{matrix}Hg{-}Cl\\Hg{-}Cl\end{matrix}+2NH_3\rightarrow\begin{matrix}Hg{-}Cl\\Hg{-}NH_2\end{matrix}+NH_4Cl$$

and later still, a mixture of finely divided mercury, and mercuric chloroamide. The evidence is as follows: If a thin layer of the black precipitate be spread on glass and dried, it will lose weight in the course of a few days, and assume a greyish-white colour. The loss in weight is explained on the assumption that the black substance is a mixture of free mercury and **mercuric chloroamide,** Cl—Hg—NH_2, and that the mercury volatilizes leaving behind the Cl—Hg—NH_2. The reaction is therefore symbolized: $2HgCl+2NH_3\rightarrow Hg+Cl.Hg.NH_2$. One proof that the black precipitate contains metallic mercury turns on the fact that if mercurous and silver chlorides be jointly precipitated and allowed to stand for some time in contact with ammonia, some metallic silver is formed by the action of the free mercury: $AgCl+Hg=Ag+HgCl$. Hence, in a qualitative analysis, "if silver be not found in the filtrate from the black precipitate, the latter should be examined for that metal." Similarly, mercurous ammonia chloride, $HgCl.NH_3$, said to be formed by the action of dry ammonia on solid mercurous chloride is really a mixture of mercury and a white precipitate, contaminated with ammonium chloride. J. G. F. Druce found the black solid does not appreciably amalgamate copper; this would favour the assumption that free mercury is not present.

The constitution of the mercury nitrogen compounds.—Many hypotheses have been suggested for the constitution of the mercury nitrogen compounds derived from ammonia, and therefore the constitutional formulæ which have been assigned to them, as well as their names, are considered to be more or less arbitrary. These compounds are insoluble in ordinary solvents, and they are decomposed by heat. Hence, their mol. wt. are a subject of conjecture rather than of demonstrated fact, and hypotheses about their constitution are proportionally vague.

C. F. Rammelsberg's diammonium theory.—C. F. Rammelsberg (1839) assumes the ammonia mercury compounds can be referred to ammonia by replacing its hydrogen atoms one by one. L. Pesci and P. C. Ray consider that all the mercury ammonia compounds can be referred to *one primary type*, dimercuriammonium, $(Hg_2N)'$, in which the four hydrogen atoms of ammonium are replaced by two atoms of bivalent mercury, and that the primary compounds have a great tendency to form double salts by union with ammonium or mercuric compounds.

K. A. Hofmann and E. C. Marburg's substituted ammonium theory.—K. A. Hofmann and E. C. Marburg (1899) and others assume that there are several primary types which can act as radicles, *e.g.*:

$[NH_2(Hg_2'')]'$	$[(N_2H_3)(Hg_2'')]''$	$[N(Hg_2'')_2]''$	$[N_2H_2(Hg_2'')_3]''$
Mercuriammonium.	Mercuridiammonium.	Dimercuriammonium.	Trimercuridiammonium.

R. J. Kane's substituted ammonia theory.—R. J. Kane (1839) assumed that these compounds are either addition products or amine- or amido-derivatives of ammonia. E. C. Franklin (1907) rejects the ammonium theories, and extends Kane's idea so as to include an interesting analogy between reactions involving ammonia and those involving water. There are ammonio-basic salts and mixed ammonio- and hydro-basic salts as well as addition compounds of ammonia.

As might be anticipated, some writers propose a compromise between these diverse views, and state that "substitution products both of ammonia and of ammonium compounds exist as well as compounds formed by the addition combination of ammonia with mercuric salts." The following, based on the work of E. C. Franklin, is convenient for purposes of classification:

Mercuric ammines.—In these compounds, the ammonia appears to be related to the metallic salt in a manner analogous with the so-called water of crystallization of ordinary hydrated salts. The compounds are formed by direct addition of the mercuric halide with ammonia. For instance, the so-called *fusible white precipitate* is an additive compound of ammonia and mercuric chloride, $HgCl_2.2NH_3$. It is formed by pouring a soln. of mercuric chloride drop by drop into a boiling soln. of ammonia and ammonium chloride as long as any of the precipitate dissolves. Rhombic crystals separate from the cooling soln. The same compound is formed when mercuric chloride is dissolved in liquid ammonia. This fusible white precipitate has been variously regarded as a **mercuric diamminochloride,** $(NH_3)_2HgCl_2$, or $HgCl_2.2NH_3$, in which ammonia plays the part of ammonia of crystallization; or as *mercuridiammonium chloride*, $NH_3Cl—Hg—NH_3Cl$; or, according to C. F. Rammelsberg, as $Hg_2NCl.3NH_4Cl$. When diamminomercuric chloride is boiled with a 20 per cent. soln. of potassium hydroxide, it is decomposed giving off, according to K. A. Hofmann and E. C. Marburg (1899), the eq. of all its nitrogen as ammonia, and according to L. Pesci (1889), three-fourths of its nitrogen as ammonia. There must be a mal-observation here. The former statement agrees with the symmetry of the nitrogen atom in the molecule and the latter with the dissymmetry of three-fourths of the nitrogen atoms in the mol. The sparing solubility of the compound is not in favour of Rammelsberg's formula. The existence of two **mercuric ammino-iodides,** $3HgI_2.4NH_3$, and $HgI_2.2NH_3$, and the ready decomposition of $HgI_2.2NH_3$ into mercuric iodide and ammonia favour the "ammonia of crystallization" theory of the constitution of fusible white precipitate. The ethylamine derivative of fusible white precipitate, **mercuric ethyldiamminochloride,** $HgCl_2.2C_2H_5NH_2$, is prepared by using ethylamine in place of ammonia. The constitutional formula for this compound is adapted to the dimercuriammonium theory of Rammelsberg—$Hg_2NCl.3NH_4Cl$—and the similarity in the mode of formation of the ethylamine and the ammonia derivatives makes it *a priori* probable that the two compounds are constituted alike. Several other derivatives of the substituted ammonias—phenylamine, benzylamine, pyridine, urea, etc.—have been similarly prepared.

When fusible white precipitate is heated, it fuses (hence the name), forming a yellow fluid which gives off some nitrogen and ammonia. As a rule, the halide derivatives decrease in stability with increasing at. wt. of the contained halogen; this is shown in the present case by the fact that the vap. press. of the ammonia in the chloride is virtually zero, while with the diamminomercuric iodide, $HgI_2(NH_3)_2$, the vap. press. of the ammonia is quite appreciable, being equal to 8 mm. of mercury at 0°; to 37 mm. at 25°; and to 601 mm. at 75°. It might be added that vap. press. measurements show no signs of the compound, $HgI_2.NH_3$; the decomposition press. of $HgI_2(NH_3)_2$ is considerable, and the compound loses ammonia on exposure to the air. Several related compounds with mercuric bromide, cyanide, sulphate, nitrate, acetate, dichromate, thiocyanate, etc., have been prepared. Some of these contain water as well as ammonia—*e.g.* $HgI_2NH_3.H_2O$.

Ammoniobasic compounds.—These compounds are formed when a soln. of mercuric chloride is treated with a slight excess of ammonia, or when mercuric chloride is poured into a large excess of ammonia. If an excess of ammonia be present in the soln. when a fusible white precipitate is being prepared ammoniolysis occurs, and a substitution product, *infusible white precipitate*, or **mercuric amidochloride,** $Hg(NH_2)Cl$, is formed: $HgCl_2.2NH_3 \rightleftharpoons NH_4Cl + Hg(NH_2)Cl$. Conversely, infusible white precipitate is converted back to fusible white precipitate by the action of a soln. of ammonium chloride in liquid ammonia. If water is present, hydrolysis as well as ammoniolysis

will simultaneously occur. Thus, fusible white precipitate, $HgCl_2.2NH_3$, is converted by ammoniolysis into infusible white precipitate, $Hg(NH_2)Cl$, as just indicated, and by hydrolysis into the so-called *Millon's base*, HgOH—NH—HgCl, by a reaction symbolized: $2NH_2HgCl+H_2O \rightleftharpoons NH_4Cl+HgOH.NH.HgCl$. The compound NH_2HgCl is regarded as an ammoniobasic salt in the same sense that HO.Hg.Cl would be regarded as a hydrobasic salt. Most of the ammoniobasic salts of the heavy metals are hydrolyzed by water, and accordingly can be formed only in soln. of liquid ammonia or of some inert solvent. The mercuric ammoniobases and salts are exceptional in their stability towards water. Hundreds have been reported as mercuriammonium compounds.

Infusible white precipitate, $NH_2.Hg.Cl$, is related to ammonia much as a basic salt, say HO.Hg.Cl, is related to water. C. F. Rammelsberg represented this compound as a double salt of dimercuriammonium chloride, $Hg_2NCl.NH_4Cl$. As evidence against this hypothesis, there is (i) the formation of a **mercuric ethylamidochloride,** $NH(C_2H_5)HgCl$, by the action of ethylamine, $NH_2(C_2H_5)$, on an excess of mercuric chloride; and the previous remarks about the ethylamine derivative of fusible white precipitate apply to the ethylamine analogue of infusible white precipitate; (ii) the sparing solubility of infusible white precipitate, an unexpected property, since the ammonium salts of the complex acid, $H(HgNCl_2)$, *nach allen analogien*, should be more soluble than is actually the case. K. A. Hofmann and E. C. Marburg consider that R. J. Kane's formula is in harmony with the fact that when boiled with an excess of 20 per cent. potash-lye, all the nitrogen is given off as ammonia. When heated, infusible white precipitate decomposes into ammonia and nitrogen without melting (hence the name), and a residue of mercurous chloride remains: $6NH_2HgCl \rightarrow N_2+4NH_3+6HgCl$. When digested with water, infusible white precipitate breaks down into ammonium chloride and an **oxydimercuricamidochloride,** OHg_2NH_2Cl. In symbols:

$$O\begin{cases} H \\ H \end{cases} + \begin{matrix} NH_2 \\ Cl \end{matrix} \begin{matrix} —Hg—Cl \\ Hg—NH_2 \end{matrix} = O\begin{matrix} Hg—Cl \\ Hg—NH_2 \end{matrix} + NH_4Cl$$

Infusible white precipitate is soluble in conc. ammonia, and when the soln. is allowed to evaporate in vacuo, over sulphuric acid, crystals separate. These when dried at 100° have a composition corresponding with what R. J. Kane regarded as NH_2HgCl.

According to N. A. E. Millon, precipitates containing the eq. of between 75 and 85 per cent. of mercury can be obtained by pouring aq. ammonia into soln. of mercuric chloride. The composition of the precipitate depends upon the temp. and conc. of the soln., on the rate of admixture, and on the amount of washing to which the precipitate is subjected. Hence, it is very probable that many mixtures have been reported as chemical compounds—mere analysis is not sufficient to establish chemical individuality.

Guided by the phase rule, D. Strömholm studied the mutual solubility of ammonium and mercuric chlorides in water, and found that four double or complex salts—(i) $HgCl.2NH_4Cl.H_2O$; (ii) $HgCl.NH_4Cl.H_2O$; (iii) $2HgCl_2.2NH_4Cl.H_2O$; (iv) $9HgCl_2.2NH_4Cl$—were stable as solid phases when the conc. of the mercuric chloride is progressively increased, and that of the ammonium chloride progressively diminished. Similarly, R. Widman (1910) has studied the conditions of equilibrium in systems containing different proportions of ammonium bromide, mercuric bromide, and ammonia, and found that the following five compounds are capable of existence: $HgBr_2.2NH_3$; NH_2HgBr; $(HgBr)_2NH$; NHg_2Br; and $Hg_9N_4Br_6$.

Millon's base.—This compound is formed in yellow rhombic crystals by the action of aq. ammonia on mercuric oxide: $2HgO+NH_4OH=(HgOH)_2NH_2OH$. Following K. A. Hofmann and E. C. Marburg, E. C. Franklin regarded Millon's base as a **dimercurihydroxyammonium hydroxide.** According to C. F. Rammelsberg's scheme, Millon's base is considered to be $Hg_2NOH.2H_2O$, where the two mols. of water play the rôle of water of crystallization. The chloride of the base

does not lose its water at 125° ; the water is lost only when the mol. breaks down completely at 180°. This agrees better with the formula $HgO(NH_2)HgCl$, or $(HgOH)_2NH_2Cl$ for the chloride of Millon's base, and with $HgO(NHg_2)HgOH$ or $(HgOH)_2NH_2OH$ for Millon's base itself. The ethylamine derivative of Millon's base, $HgOH.N(C_2H_5)HgCl$, like the ethylamine derivative of fusible and infusible white precipitates, is cited as an argument in favour of the constitutional formulæ $HgOH.NH.HgCl$. E. Weitz (1915) represents the relation between these three compounds as follows :

$(NH_3)_2HgCl_2$ → $(NH_2)HgCl$ → $HgO(NH_2)HgCl$

Fusible precipitate. Infusible precipitate. Chloride of Millon's base.

which implies hydrolytic actions with $NH_3.Hg(OH)Cl$ as an intermediate product. The hydrolysis of the infusible precipitate which furnishes mercuric oxide and ammonium chloride, proceeds $NH_2HgCl+H_2O \rightleftharpoons HgO+NH_4Cl$, and the mercuric oxide unites with a second mol. of NH_2HgCl to form the chloride of Millon's base. According to this view, Millon's base is constituted $HgO.(NH_2)HgOH$.

When Millon's base is boiled with potash-lye, it loses a mol. of water to form the so-called *first anhydride of Millon's base*, a feebly explosive compound, represented as $2HgO.NH_3$, or $O\langle{}^{Hg}_{Hg}\rangle N\langle{}^{H_2}_{OH}$, or, according to E. C. Franklin, $HgOH.NH.HgOH$. E. C. Franklin likens this reaction to the hydration of a metallic oxide to a hydroxide in virtue of the marked tendency of mercury to replace hydrogen in many of the derivatives of ammonia. Water reacts with calcium oxide to form calcium hydroxide, but ammonia, in the absence of water, reacts with mercuric oxide to form not $HO.HgNH_2$, but rather a derivative of this, *viz.* $(HOHg)_2NH$, and this reacts with water, forming Millon's base, $(HOHg)_2NH_2OH$. With Franklin's formula, the basic properties of the first anhydride are referred to the characteristic, slightly basic, properties of mercuric hydroxide, and with K. A. Hofmann and E. C. Marburg's formula, to the persistence of the properties of the contained ammonia. The former hypothesis agrees better with the characteristic tendency of halogens to unite with mercuric compounds. A *second anhydride of Millon's base* is represented by the empirical formula Hg_2NOH, and Franklin's graphic formulæ for these compounds are :

$HO—Hg\rangle N\langle{}^{H_2}_{OH}$ → $HO—Hg\rangle NH$ → $HO—Hg\rangle N$

$HO—Hg$ $HO—Hg$ Hg

Millon's base. First anhydride. Second anhydride.

This view is in accord with the action of dil. acids on hydroxyl bases, converting them into basic salts, *e.g.* the chloride of Millon's base $HgOH—NH—HgCl$; while more conc. acids change them into neutral salts, *e.g.* $HgCl—NH—HgCl$, is made by the action of aq. ammonia on an excess of a boiling soln. of mercuric chloride.

Salts of Millon's base.—In addition to the chloride, various other salts of Millon's base have been prepared—bromide, iodide, fluoride, bromate, sulphate, nitrate, carbonate, cyanide, thiocyanate, etc. The action of ammonia on mercuric sulphate, of a soln. of ammonium sulphate on mercuric oxide or basic mercuric sulphate, or of dil. sulphuric acid on Millon's base, furnishes a white powder which has been obtained in octahedral crystals. This compound is the sulphate of Millon's base, and has been called *ammonia turpeth ;* it has the empirical formula $Hg_4N_2H_4O_8$, or graphically, $HgOH.NH.HgSO_4.HgNH.HgOH$. It does not lose water when heated to 115°. When mercuric nitrate is dissolved in a boiling soln. of ammonium nitrate, the cooling soln. deposits needle-like crystals with the empirical formula $Hg_2N_3H_{12}O_2.3NO_3$, which is usually dissected into $Hg(NO_3)_2.2NH_3.2H_2O.NH_2HgNO_3$, and called *Kane's salt* because it was first prepared by R. J. Kane. Another nitrate called *Mitscherlich's salt* is supposed to have the composition $NH_2HgNO_3.HOHgNH.HgNO_3$, and is prepared by treating a dil. barely acid soln. of mercuric nitrate with dil. aq. ammonia—not in excess. The nitrate of Millon's base, called

Soubeiran's salt, $HgOH—NH—HgNO_3$, is prepared by the action of a slight excess of ammonia on a dil. soln. of mercuric nitrate; by the action of boiling water on Mitscherlich's salt, or of water on Kane's salt. Several other nitrates have been reported; they can all be regarded as products of hydrolysis and ammoniolysis.

In view of the fact that the systematic name for these compounds is dependent upon the particular hypothesis employed as to their constitution, there is an advantage in employing such unsystematic arbitrary names as Millon's base, fusible and infusible white precipitate, etc., for the names do not then change with a change in fashion or mode of viewing their constitution.

By the action of an excess of conc. ammonia on mercuric iodide, or the action of Nessler's reagent on ammonia, a brownish precipitate **mercurihydroxyimidoiodide,** HgOH—NH—I, is formed (Nessler's reaction). When Millon's base is heated in a stream of ammonia, a dark brown explosive compound, Hg_2NOH, or graphically HOHg—N=Hg, is formed by the loss of two mols. of water, and the anhydrous oxide, $(Hg_2N)_2O$, has been made. A compound with the empirical formula NHg_2I is precipitated when a soln. of potassamide is mixed with an excess of, say, mercuric iodide dissolved in liquid ammonia. Its constitution is probably **mercuric iodonitride,** HgN—Hg—I, and not dimercuric ammonium iodide. It appears to be a relation of $NH_2.Hg.I$ obtained by replacing two atoms of hydrogen by bivalent mercury. A similar **mercuric bromonitride,** NHg_2Br, has been prepared.

Hydroxylamine, NH_2OH, and hydrazine, N_2H_4, form addition products with mercuric chloride. With water, the hydrazine compound splits off hydrazine chloride, $N_2H_4.HCl$, and forms $HgCl.NH.NH.HgCl$, or $(HgCl)_2N_2H_2$, in the same way that fusible white precipitate splits off ammonium chloride and forms infusible white precipitate. A series of mercuriphosphorus bases has been made by K. A. Aschan (1886), and of mercuriarsenic bases by A. Partheil and E. Amort (1898) analogous with the mercuric nitrogen compounds. Thus, Hg=H—HgCl is analogous with Hg=P—HgCl; and $NH(HgCl)_2$ with $AsH(HgCl)_2$.

A series of products has been obtained in which the hydrogen of the hypothetical ammonium oxide, $(NH_4)_2O$, is replaced by bivalent mercury, thus furnishing the mono- and tetra-hydrates of dimercuriammonium oxide, $(NHg_2)_2O.H_2O$, $(NHg_2)_2O.4H_2O$; the anhydrous oxide and the di-, tri-, and penta-hydrates are probably doubtful. There is also a dimercuriammonium monamminoxide, $(NHg_2)_2O.NH_3$.

W. Weyl [2] claimed to have made anhydrous **dimercuriammonium oxide**, $(NHg_2)_2O$, by the action of liquid ammonia on mercuric oxide contained in one leg of a sealed W-tube, silver chloride sat. with ammonia being warmed in the other leg; and also by warming the trihydrate, and keeping the trihydrate over sulphuric acid. H. Gaudechon claimed to have made it by the action of dry ammonia on the monohydrate between 100° and 110°. W. Weyl thinks that the mercuric nitride prepared by C. H. Hirzel by the action of ammonia on precipitated mercuric oxide is this compound. K. A. Hofmann and E. C. Marburg could not get a product with less combined water than NHg_2OH by the action of ammonia on mercuric oxide at 125° for 3 hrs. E. C. Franklin represents this compound by the formula: Hg : N.Hg.O. Hg.N : Hg, but he doubts if it has yet been prepared. According to H. Gaudechon, the heat of formation from the elements is −75·3 to 76·6 Cals., and the heat of neutralization of the solid with hydrochloric acid is $(NHg_2)_2O+2HCl=(NHg_2Cl)_2 H_2O+52·9$ Cals. The compound is not soluble in liquid ammonia. It explodes violently by heat, percussion, or friction. It explodes when warmed in hydrogen; it hydrates rapidly in humid air free from carbon dioxide; it absorbs carbon dioxide very slowly, forming a crust of carbonate; it is completely decomposed by water at 100° into mercuric oxide and ammonia; likewise also the dissolution of potassium chloride or hydroxide; hydrogen chloride rapidly acts on the dry compound that is formed, and mercuric and ammonium chlorides are formed. According to W. Weyl, hydrochloric or nitric acid dissolves it without residue, but, according to H. Gaudechon, it is not completely soluble in hydrochloric acid since some mercurous chloride

is formed. W. Weyl found that it is dissolved by a soln. of potassium cyanide at 130°.

W. Weyl prepared **monohydrated dimercuriammonium oxide,** $(NHg_2)_2O.H_2O$, or NHg_2OH, by dehydrating the trihydrate in a stream of ammonia; K. A. Hofmann and E. C. Marburg, by heating Millon's base (*vide infra*) to 125° in a stream of ammonia, or by heating dry yellow mercuric oxide to 120° in ammonia; H. Gaudechon, by heating the tetrahydrate under diminished pressure in the presence of barium oxide, or by heating the tetrahydrate to 40° or 50° in a stream of dry ammonia. C. F. Rammelsberg kept dimercuric hemiammoniodioxide, $2HgO.NH_3$, or $NHg_3OH.H_2O$, over quicklime. E. C. Franklin represented its constitution by the formula Hg : N.Hg.OH; W. Weyl, by $(NHg_2)_2O.3H_2O$; H. Fürth, by O : Hg_2 : $NH.H_2O$; and K. A. Hofmann and E. C. Marburg, by HO.N : $Hg_2.H_2O$. The last-named gave 8·52 for the sp. gr. H. Gaudechon gave for the heat of formation $(NHg_2)_2O+H_2O_{solid}=(NHg_2)_2O.H_2O+1·6$ Cals. K. A. Hofmann and E. C. Marburg found that this compound can be preserved in closed vessels; but all observers agree that the compound is explosive; and W. Weyl said that the brown flocculent powder is less stable than the trihydrate; H. Gaudechon, that it is stable in air up to 20°, and at 50° no ammonia is lost. C. F. Rammelsberg found that ammonia is not lost either over sulphuric acid or over phosphorus pentoxide, although about 4·01 per cent. of water is given off, and that it probably forms at a higher temp., $(NHg_2)_2O$, and mercuric oxide and mercuric nitride, when heated still more. W. Weyl stated that under water it forms the trihydrate; and H. Gaudechon, that in water vapour free from carbon dioxide at 10° or 20° and about 10 mm. press., it gradually absorbs water, forming the tetrahydrate. K. A. Hofmann and E. C. Marburg stated that the compound gradually absorbs moisture from the air, and becomes non-explosive. W. Weyl found that it is easily soluble in hydrochloric acid; K. A. Hofmann and E. C. Marburg, that while it is soluble in dil. hydrochloric acid, a conc. soln. of hydrogen chloride in ether does not attack it, for the group NHg_2OH does not seem to be able to unite with acid radicles. H. Gaudechon found liquid ammonia converts it slowly into garnet-red **dimercuriammonium amminoxide,** $(NHg_2)_2O.NH_3$, when the excess of ammonia is removed at −21°. It is stable at −21° under a press. of 750 mm. of mercury.

The so-called *dihydrated dimercuriammonium oxide,* $(NHg_2)_2O.2H_2O$, was reported by N. A. E. Millon as a product of the dehydration of the tetrahydrate; and he added that the brown mass could be heated without explosion; that it is insoluble in water or alcohol; that it is scarcely attacked by boiling conc. potassium hydroxide, but is decomposed by the molten hydroxide into nitrogen, mercury, and mercuric oxide; that with a hot soln. of ammonium nitrate chloride, sulphate, acetate, or oxalate, ammonia is evolved; and that water decomposes it into a green compound. E. C. Franklin and H. Gaudechon believe that N. A. E. Millon was mistaken in assuming that his product is the dihydrate in question, and H. Gaudechon also said that it is very unlikely that *trihydrated dimercuriammonium oxide,* $(NHg)_2O.3H_2O$, exists, although C. F. Rammelsberg gave it the formula NHg.NOH.HgOH, which E. C. Franklin believes is improbable; K. A. Hofmann and E. C. Marburg give O : Hg_2 : N ⋮ $H_2(OH)$; and H. Fürth, HO.Hg.O.Hg.NH_3. N. A. E. Millon and C. H. Hirzel obtained what they regarded as the trihydrate by drying the higher hydrate over sulphuric acid; K. A. Hofmann and E. C. Marburg, by drying Millon's base, protected from light, in an atm. of ammonia, over potassium hydroxide; C. F. Rammelsberg, by drying the hydrate, $(NHg_2)_2O.4\frac{1}{2}H_2O$, over potassium hydroxide, calcium oxide, sulphuric acid, or phosphorus pentoxide, and also by the action of dry ammonia on yellow mercuric oxide; and W. Weyl, by shaking mercuric oxide for some hours with alcoholic ammonia, and drying it in air at ordinary temp., or by saturating yellow mercuric oxide with ammonia at ordinary temp., grinding the product, and again saturating with ammonia. If the press. of the ammonia be $2\frac{1}{2}$ atm. the action proceeds much more quickly. The general behaviour of the brown product is very much like that of the higher hydrate.

H. Gerresheim prepared **tetrahydrated dimercuriammonium oxide,** $(NHg_2)_2O.4H_2O$, by allowing freshly precipitated mercuric oxide, free from alkali, to stand for several days at 40°–60° in aq. ammonia, free from carbon dioxide. The aq. ammonia is decanted off, and the product is washed first with alcohol, then with

ether, and rapidly dried. H. Gaudechon used a somewhat similar process, and he also exposed the monohydrate to water vapour as previously indicated; he obtained greenish-yellow crystals, and gave for the heat of formation $4HgO+2NH_{3aq.}+H_2O=(NHg_2)_2O.4H_2O+14{\cdot}4$ Cals. According to H. Gerresheim, the yellow powder becomes superficially grey when exposed to light for some time. It crackles continuously when rubbed in a mortar; when exposed to dry air, or when heated to 50°–60°, it becomes brown and loses water; when heated to a higher temp. it decomposes—explosively if the rise of temp. be rapid. H. Gaudechon found that this compound becomes brown in vacuo over phosphorus pentoxide, and forms the monohydrate—some nitrogen is also given off; he added that the tetrahydrate is stable only in the presence of water vapour and ammonia. H. Gerresheim found the tetrahydrate to be slightly soluble in water, a litre of water at 17° dissolving 0·077 grm. of the tetrahydrate, and at 80°, 0·588 grm. Minute crystals are obtained on cooling the sat. soln.

The tetrahydrate was found by H. Gaudechon to be stable in water free from carbon dioxide, but at 100° it is gradually decomposed with the formation of mercuric oxide—and this in platinum vessels so that it is not an effect of alkali in the glass; if carbon dioxide be present, mercuric carbonate is formed, and a skin of the carbonate protects the tetrahydrate from the action of the water. The reaction is thought to be reversible: $(NHg_2)_2O.4H_2O \rightleftharpoons 4HgO+2NH_3+H_2O$, since on cooling, the ammonia left in soln. slowly recombines with the mercuric oxide. Liquid ammonia reacts with the tetrahydrate, forming in the course of a few days a garnet-red compound—possibly $(NHg)_2O.NH_3$, *vide supra*. According to H. Gaudechon and H. Gerresheim, a soln. of potassium hydroxide does not act on the tetrahydrate, and when it decomposes in a boiling soln. of this alkali, the decomposition is thermal not chemical. The latter obtained a brown explosive product by evaporating the tetrahydrate with a soln. of potassium hydroxide, and he added that nitric acid converts it into a white insoluble salt; hydrochloric acid gives a white chloride soluble in excess of the acid; dil. sulphuric acid forms an insoluble sulphate; conc. sulphuric acid colours it brown; and acetic acid yields a soluble acetate. The sulphate and nitrate are not precipitated from the soln. of the salt, and it is thought that in these salts the arrangement of the atoms is different from that in the original, because of the difference in their behaviour towards hydrochloroplatinic acid. With soln. of various salts, the tetrahydrate seems to unite with the acid radicle without the base passing into soln., and if an excess of the salt is present, the base dissolves if a soluble double salt is formed—*e.g.* most ammonium salts—or it dissolves with decomposition—*e.g.* potassium iodide, cyanide, or ferrocyanide, or sodium sulphide—or it remains undissolved—*e.g.* most salts. H. Gerresheim also studied the action of ethyl bromide and iodide, which form the iodide of the base; chloroform, which forms a gas, the chloride, and the formate of the base; and carbon disulphide, which forms the thiocarbonate of the base.

C. F. Rammelsberg obtained a hygroscopic pale yellow powder by the action of aq. ammonia on mercuric oxide; its composition was between $2HgO.NH_3.H_2O$ and $2HgO.NH_3.\frac{1}{2}H_2O$, or *hemiennahydrated dimercuriammonium oxide*, $(NHg_2)_2O.4\frac{1}{2}H_2O$. The general properties resemble those of the other hydrates. L. J. Proust, and P. Plantamour prepared what has been regarded as *pentahydrated dimercuriammonium oxide*, $(NHg_2)_2O.5H_2O$, by digesting mercuric oxide with a warm aq. soln. of ammonia free from carbonate. R. J. Kane, C. H. Hirzel, and N. A. E. Millon studied the reaction. The last-named also obtained the pentahydrate by warming dimercuriammonium salts with alkali hydroxide; and H. Fürth, by precipitating mercuric acetamide with aq. ammonia. The latter represented the constitution of the salt by $HOHg.O.Hg.NH_3OH$; K. A. Hofmann and E. C. Marburg, as $(HgOH)_2NH_2OH$, not as $NHg_2OH.2H_2O$; E. C. Franklin, as a mixed hydro-ammonio-base, $2HgO.NH_3.H_2O$, or $Hg(OH)_2.Hg(NH_2)OH.3Hg(OH)_2.Hg(NH_2)_2$; and later, as $HO.Hg.NH.Hg.OH.H_2O$. H. Gaudechon said that if this compound exists at all, it is unstable at 0°, since the tetrahydrate does not take up an appreciable amount of water, if kept 8 days at 0° in an atm. sat. with water vapour. According to J. L. Proust, P. Plantamour, R. J. Kane, and N. A. E. Millon, the pale yellow powder decomposes on exposure to light; it decrepitates without explosion when rubbed in a mortar, but at a dull red heat, it explodes not so vigorously as fulminating gold. When confined over

sulphuric acid C. H. Hirzel found that it lost nearly the eq. of $2H_2O$, and N. A. E. Millon, that it lost at 130° nearly the eq. of $3H_2O$, and that the product obtained with yellow mercuric oxide loses its water more readily than that prepared from the red oxide. K. A. Hofmann and E. C. Marburg found that it loses the eq. of H_2O over potassium hydroxide, and thereby becomes less stable and loses ammonia; absolute alcohol was also found to abstract water, forming a brown substance, which becomes yellow and then gradually decomposes into mercuric oxide, water, and ammonia. E. C. Franklin represents the dehydration changes: $(HgOH_2) : NH.H_2O \rightarrow HgOH.NH.HgOH \rightarrow HgOH.N : Hg$. R. J. Kane found that when heated it decomposes into ammonia, nitrogen, mercuric oxide, and water vapour. N. A. E. Millon and G. C. Wittstein said that the pentahydrate is insoluble in water or alcohol; and that aq. ammonia dissolves only traces; the former found that a cold soln. of potassium hydroxide does not attack the pentahydrate, but with a boiling soln. incomplete decomposition occurs, and ammonia is evolved; it attracts moisture from the air; it forms salt-like products with acids; and behaves like the dihydrate with soln. of ammonium salts. P. Plantamour obtained a brownish powder by the action of dry ammonia at 150°.

The so-called *Millon's base* is an ammonio-hydroxy-base, **dimercurihydroxy-ammonium hydroxide,** $(HgOH)_2.NH_2OH$, or $HgOH.NH.HgOH.H_2O$. According to E. C. Franklin, the simplest ammonio-hydroxy-base is $NH_2.Hg.OH$ intermediate between HO.Hg.OH, and $NH_2.Hg.NH_2$, but it has not yet been isolated; Millon's base may be regarded as being formed from this hypothetical base by the loss of ammonia: $2(NH_2.Hg.OH) = HgOH.NH.HgOH + NH_3$. The product of the action of aq. ammonia on mercuric oxide contains one or one-and-a-half mol. of water. H. Gerresheim obtained yellow crystals of the base by keeping mercuric oxide and aq. ammonia in a sealed vessel for six months. K. A. Hofmann and E. C. Marburg digested for 12 hours. in darkness mercuric oxide, precipitated at 70°, with an aq. soln. of ammonia, free from carbon dioxide; the product was dried by suction and washing with absolute alcohol and ether. H. Gaudechon always found Millon's base to be contaminated with a little carbonate. H. Endemann and G. A. Prochaza recommended washing out the hydrochloric acid, sulphuric acid, carbon dioxide, and silica by a soln. of normal sodium carbonate. When Millon's base is dried in vacuo over sulphuric acid, there remains a dark brown non-explosive product assumed to have the composition NHg_3O_2H, but which is probably a mixture. The general properties of Millon's base were shown by E. C. Franklin to be such as might have been anticipated by his views of its constitution. K. A. Hofmann and E. C. Marburg gave 4·083 for the sp. gr. at 18°. The salts of Millon's base are slowly decomposed when heated with potassium hydroxide, and they are scarcely soluble in 10 per cent. nitric, sulphuric, or acetic acid, and H. Gerresheim was able to crystallize salts of Millon's base from acetic acid soln. F. L. Sonnenschein, and E. Enss showed that ethyl iodide reacts with the salts of Millon's base, forming primary amines.

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§ 9. Mercurous Fluoride

Mercury forms two fluorides—mercurous fluoride, HgF; and mercuric fluoride, HgF_2. J. L. Gay Lussac and L. J. Thénard [1] reported in 1811 that hydrofluoric acid does not react with mercury at any temp.; and J. J. Berzelius said that if hydrofluoric acid be added to a soln. of mercurous nitrate, no signs of precipitation occur, and when the soln. is evaporated, the hydrofluoric acid volatilizes leaving the original nitrate as a residue. H. Moissan found that mercury absorbs fluorine at ordinary temp., forming pale yellow mercurous fluoride; he also said that the same salt is formed by the action of fluorine on moderately heated mercuric oxide, but no evidence was advanced as to the purity of the product. J. J. Berzelius obtained mercurous fluoride by double decomposition by heating an intimate mixture of mercurous chloride and sodium fluoride in a matrass; the sublimate of mercurous fluoride must have been contaminated with chloride. J. J. Berzelius did not succeed in making mercurous fluoride by heating mercuric fluoride with mercury. R. Finkener prepared mercurous fluoride by adding freshly precipitated mercurous chloride to an excess of a soln. of silver fluoride: $AgF+HgCl=AgCl+HgF$, and on evaporating the clear liquid, small yellow crystals of mercurous fluoride appeared; he also prepared the same salt more readily by the action of hydrofluoric acid on recently precipitated mercurous carbonate. Hydrofluoric acid attacks mercurous oxide very slowly.

Mercurous fluoride forms pale yellow crystals—possibly cubic—which are stable in dry air and which can be heated to about 260° without change, but at higher temp. the salt sublimes, and the glass containing vessel is simultaneously etched. H. Moissan says that when heated in glass vessels, mercury and silicon tetrafluoride are formed. If exposed to humid air, or to light, the crystals are blackened. According to R. Finkener, the salt is partially decomposed by water into mercurous oxide and hydrofluoric acid, and part seems to dissolve as mercurous fluoride. J. J. Berzelius probably made an impure mercurous fluoride, for he stated the salt is white and insoluble in water. Mercurous fluoride dissolves in nitric acid, and the salt is precipitated from its soln. in dil. hydrofluoric acid by "salting" with potassium fluoride; the precipitate retains some acid potassium fluoride, KHF_2, very tenaciously, and this salt can be removed only by prolonged washing. Mercurous fluoride is blackened by ammonia gas, forming what R. Finkener thought to be **mercurous ammino-fluoride,** $HgF.NH_3$, which gives off ammonia at 100°. The addition of potassium hydroxide to a soln. of mercurous fluoride in hydrofluoric acid precipitates a black-coloured oxide. Mercurous fluoride gradually absorbs dry ammonia gas—the absorption of 7·63 per cent. occupied two days. The product is black. Aqua ammonia also gives a black precipitate which becomes grey on standing some time. The black precipitate is probably a mixture of mercuric oxide and mercury, and not as was once supposed *mercurous ammino-fluoride*, $HgF.NH_3$, for as R. Finkener showed: (i) nitric acid develops nitric oxide and forms mercurous nitrate, leaving white mercuric oxide as a residue, and if dry mercurous fluoride be vigorously agitated with aqua ammonia, dil. nitric acid removes about half of the employed mercury; (ii) if ammonia be added to a dil. soln. of mercurous fluoride in hydrofluoric acid, but not to neutralize completely

the acid, the filtered liquid furnishes mercuric oxide, and the precipitate when dried in darkness at ordinary temp. contains metallic mercury. E. Böhm obtained colourless, prismatic monoclinic crystals of **mercurous hydrofluoride,** $HgF.2HF.2H_2O$, with axial ratios $a : b : c = 0{\cdot}5673 : 1 : 1{\cdot}060$, and $\beta = 105° 10'$, by dissolving freshly precipitated and well-washed mercuric oxide in hot conc. hydrofluoric acid, and evaporating the filtrate in vacuo over sulphuric acid. The crystals are fairly stable in dry hydrofluoric acid, and less stable over sulphuric acid in vacuo. When heated to redness, mercurous fluoride decomposes without melting, forming mercuric oxide and hydrogen fluoride. The crystals are hygroscopic in moist air; and they become white and opaque. The salt is soluble in water and dilute acids; the aq. soln. is blackened by alkali-lye; and, according to J. Philippi, it gives a white precipitate of mercuric thiocyanate, $Hg(SCy)_2$, with potassium thiocyanate.

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§ 10. Mercuric Fluoride

J. L. Gay Lussac and L. J. Thénard,[1] and J. J. Berzelius prepared a pale orange-yellow powder by the action of hydrofluoric acid on mercuric oxide. The powder dissolves in water, forming a colourless soln. which, on evaporation, furnishes dark yellow prisms which were thought to be crystals of mercuric fluoride. E. Frémy also obtained colourless needle-like crystals of a hydrated mercuric fluoride from the soln. obtained by the action of conc. hydrofluoric acid on mercury. In all these cases, R. Finkener believed that not mercuric fluoride, but rather **mercuric oxyfluoride,** $HgO.HgF_2.H_2O$, or $Hg(OH)F$, is formed. This compound does not change at 100°, but at a higher temp. the product darkens and gives off moisture and hydrofluoric acid which attacks glass; the compound finally melts and furnishes mercury. The oxyfluoride resembles mercurous fluoride in its action on water; it is soluble in dil. nitric acid.

According to O. Ruff and G. Bahlau, if mercurous fluoride or mercuric chloro-fluoride—*vide infra*—be heated in chlorine to 275°, mercuric chloride sublimes, and anhydrous mercuric fluoride remains. Similarly, if mercurous fluoride or mercuric bromofluoride be heated in a stream of bromine at 400°, mercuric bromide sublimes and anhydrous mercuric fluoride remains, but in this case a loss of mercuric fluoride by sublimation occurs. If mercurous fluoride be heated at 450° and 10 mm. press., transparent octahedral crystals of anhydrous mercuric fluoride are formed.

According to R. Finkener, **dihydrated mercuric fluoride,** $HgF_2.2H_2O$, can be made by the action of a large excess of 50 per cent. hydrofluoric acid on dry mercuric oxide. The product is a white solid contaminated with a little mercuric oxide. It is soluble in dil. nitric acid. When the solid is dehydrated it loses hydrofluoric acid, and either a mixture of mercuric oxide and mercuric fluoride or oxyfluoride, is formed. This salt is not altered by exposure to dry air or to light. Mercuric fluoride is largely hydrolyzed in aq. soln.: $HgF_2 + H_2O \rightleftharpoons HgO + H_2F_2$. A. Jäger

and A. J. Cox found the solubilities of mercuric oxide in hydrofluoric acid of different conc. to be :

TABLE IX.—HYDROLYSIS OF MERCURIC FLUORIDE.

Normality of hydrofluoric acid.	Gram atoms mercury per 1000 c.c.		Ratio found : Calculated.
	Found.	Calculated.	
0·12	0·01258	0·06	0·21
0·24	0·0247	0·12	0·20
0·57	0·0629	0·285	0·22
1·11	0·1168	0·555	0·21
1·14	0·1197	0·568	0·21
2·17	0·2586	0·185	0·24

The calculated value is based on the assumption that HgO is eq. to H_2F_2. A. Jäger found the solubility of mercuric oxide in hydrofluoric acid to be lowered in the presence of potassium fluoride, owing to the decrease in the conc. of the acid by the formation of KHF_2. R. Abegg and A. J. Cox estimate the ionization constant of mercuric fluoride: $HgF_2=Hg^{\cdot\cdot}+F_2''$, to be about 260 times as great as the unknown ionization constant of hydrofluoric acid : $H_2F_2=2H^{\cdot}+F_2''$.

A. J. Cox found that in the system : mercuric oxide, hydrofluoric acid, and water, as the conc. of the acid diminishes, the composition of the soln. remains constant, while the composition of the precipitate varies. Under these conditions, two solid phases are present—a mixture of mercuric oxide and fluoride—but the analyses give no indication of the presence of a basic mercuric fluoride. At 25° the minimum conc. of the hydrofluoric acid necessary for the existence of mercuric fluoride in soln. is 1·14*N*-HF. This shows that quite apart from the conc. of the acid, the yield of salt is only 0·22 of the theoretical, consequently, about 78 per cent. of the salt is hydrolyzed. This illustrates the difficulty, nay the impossibility—as C. Poulenc expresses it—of preparing anhydrous mercuric fluoride in the wet way.

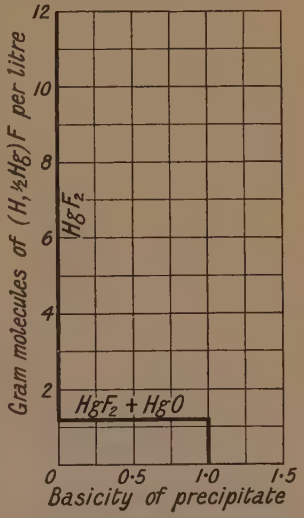

FIG. 10.—Relation between Composition of the Precipitate and of the Solution at 25°.

O. Ruff and G. Bahlau's anhydrous mercuric fluoride forms transparent octahedral **crystals** of sp. gr. 8·95 (15°); m.p. 645°; and **boiling point** 650° (estimated). Attempts to determine the **vapour tension** at various temp. did not yield satisfactory results, since the vessels are attacked by the vapours. The substance is very sensitive to moisture and becomes discoloured by traces of water vapour, which are not analytically demonstrable; on exposure to air, hydrogen fluoride is evolved, and mercuric oxyfluoride and, ultimately, mercuric oxide remain. With small quantities of water, a white, hydrated oxyfluoride, $Hg_3F_4(OH)_2$, $3H_2O$, is formed, whilst with larger quantities, mercuric oxide is gradually produced. Mercuric fluoride dissolves in 40 per cent. hydrofluoric acid soln., and, on cautious evaporation, R. Finkener's dihydrated fluoride, HgF_2, $2H_2O$, is obtained in small, colourless crystals. The vapours of mercuric fluoride attack platinum above 500°; mixtures of the fluoride with silver, copper, lead, aluminium, magnesium, zinc, tin, chromium, iron, or arsenic react vigorously when strongly heated locally, yielding

amalgams and metallic fluorides, the latter being easily obtained in a high degree of purity, if an excess of mercuric fluoride is used. Sulphur tetrafluoride appears to be formed when mercuric fluoride is heated with sulphur, but no reaction occurs with amorphous or graphitic carbon. The fluorine does not appear to be replaced when mercuric fluoride is heated in a stream of chlorine or bromine. However, if dry chlorine be passed over mercurous fluoride at 120°, O. Ruff and G. Bahlau said that pale yellow **mercuric fluochloride,** HgClF, is formed; and with bromine at 105° pale yellow **mercuric fluobromide,** HgFBr. H. Moissan made the former compound by passing a current of dry chlorine over the product obtained by heating E. Frémy's $HgF_2.2H_2O$ to 350°, and drying by contact with anhydrous hydrofluoric acid.

E. Böhm prepared the fluorine analogue of infusible white precipitate (*q.v.*) with the composition $HgF.NH_2$, and which E. C. Franklin called **mercuric fluoroamide,** NH_2—Hg—F, or $Hg(NH_2)F$, by mixing 200 grms. of conc. hydrofluoric acid with an excess of yellow mercuric oxide, and adding an excess of ammonia to the filtered soln. A pale yellow amorphous powder separated when alcohol was added. This was washed with alcohol and ether, and dried over sulphuric acid in vacuo in darkness. When exposed to light the surface of the powder is coloured grey, owing to the separation of mercury; it is insoluble in water, and in nitric and sulphuric acids, but is readily soluble in dil. hydrochloric acid. When heated in a tube, it sublimes with partial decomposition.

R. Finkener reported the formation of a white pulverulent compound, $NHg_2F.HF.H_2O$, by the addition of a small excess of ammonia to a soln. of mercuric fluoride in hydrofluoric acid; on standing in the cold a white gelatinous mass separates gradually—rapidly when heated—it can be washed without decomposition, and dried over sulphuric acid. On the ammonium theory, the compound is called *oxydimercuri-ammonium fluoride,* and represented $NH_2(Hg.O.Hg)F.HF$, while in E. C. Franklin's nomenclature it is **mercuric difluoroamide,** $(HgF)_2NH.H_2O$. According to R. Finkener, when heated with lead oxide in a glass tube to about 200°, this compound decomposes: $6PbO+6(NHg_2F.HF.H_2O)=6PbF_2+9HgO+3Hg+3H_2O+4NH_3+N_2$.

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§ 11. Mercurous Chloride

Mercury forms two chlorides, calomel or mercurous chloride, HgCl, and corrosive sublimate or mercuric chloride, $HgCl_2$. Both appear to have been known under various names for quite a long time, although the discoverer of either is unknown. A. M. Rhases mentioned corrosive sublimate in the tenth century, and E. S. Avicenna in the eleventh century. We are also told that it was known to the Chinese. H. Kopp, in his *Geschichte der Chemie* (Braunschweig, 1847), has reviewed the history of the mercury chlorides. In the thirteenth-century works of the Latin Geber, *De inventione veritatis,* and of Albertus Magnus, *Compositum de compositis,* there are descriptions of a method of preparing *album sublimatum,* by sublimation in an aludel, from an intimate mixture of mercury, rock alum, common salt, and saltpetre. The—presumably—sixteenth- or seventeenth-century works of Basil

Valentine have also much to say on the preparation of *mercurius sublimatus*, and at that time it appears to have been an article of commerce. Since mercurous chloride is formed if mercury be in excess, the older preparations must frequently have been mixtures of both mercury chlorides, and the term was for some time applied to these two salts. The corrosive properties of mercuric chloride led to its being called *draco, mors metallorum*, or *malleus metallorum* on account of its destroying, "deadening," or "sickening," the metallic lustre of many metals; it was also called *mercurous sublimatus corrosivus*, or simply *corrosive sublimate*. The old synonyms for the two mercury chlorides have been tabulated in G. F. Hildebrandt's *Chemische und mineralogische Geschichte des Quecksilbers* (Braunschweig, 1793).

Basil Valentine [1] mentions the preparation of *mercurius sublimatus* by sublimation from a mixture of vitriol, common salt, and mercury, and he says that during the operation, the spirit of salt (hydrochloric acid) unites with the mercury. N. Lemery described its preparation from mercury nitrate, common salt, and calcined vitriol; and O. Tachen (1666) gave a minute description of the process employed in Venice and in Amsterdam for the preparation of corrosive sublimate. J. Kunckel (1716) and G. F. Boulduc (1730) prepared the salt by sublimation from a mixture of mercury sulphate and common salt. A. G. Monnet (1771) made it in the wet way by mixing common salt with a soln. of a mercuric salt, or by cooling a hot soln. of mercury in a mixture of nitric and hydrochloric acids. Indeed, T. Bergman (1781) enumerated fourteen methods of preparing this salt. J. Beguin said that corrosive sublimate sublimes more rapidly and the product is denser if some arsenic be present. C. Glaser (1663), R. Boyle (1661), and N. Lemery (1675) also refer to the adulteration of corrosive sublimate with arsenic.

Mercurous chloride was used medicinally in the sixteenth century. It was sometimes designated *panchymachogum Quercetani*, *panchymachogum minerale*, *panacea mercurialis*, *panacea cœlestis*, etc. A. Libavius (1597) called it *aquila alba*, and J. Beguin (1608) and O. Croll (1609) called it *draco mitigatus*, or *manna metallorum*; F. Sylvius de la Böe (1671), *mercurius dulcis*; and N. Lemery (1675), *sublimé doux*. From this it would appear as if the early impure preparations had a sweet taste, although the compound itself is tasteless. The term *calomel*—from καλός, good; and μέλι, sweet, in reference to its name *mercurius dulcis*; or from καλός, good; μέλας, black—possibly refers to the blackening which this salt suffers when treated with an alkali; to its use as a good remedy for black bile; or to the general regard for black mercury sulphide to which the name calomel was first applied.

O. Croll (1609), near the beginning of the seventeenth century, spoke of the secrecy and mystery of the process of preparing this salt, and J. Beguin (1608) referred to its preparation from *mercurius sublimatus*, mercury, and red oxide of iron. J. le Mort (1696) first mentioned its preparation from mercury, salt, and calcined vitriol, without *mercurius sublimatus*; and J. Zwelfer (1652) mentioned the purification of this salt by washing out the corrosive sublimate with water. In the fourteenth century, J. de Roquetaillade first described the preparation of calomel in the wet way as a precipitate by adding sal ammoniac to a soln. of mercury in nitric acid—the calomel was afterwards purified by sublimation—and N. Lemery (1675) used salt, or hydrochloric acid, and called the product *le precipité blanc*; H. Boerhaave (1732), *mercurius precipitatus albus*; and J. Kunckel (1716), *lac mercurii*. C. Neumann (1740) stated that the precipitate obtained in this way is the same as *mercurius dulcis* prepared by sublimation, and C. W. Scheele (1778) confirmed C. Neumann's hypothesis. This method of preparation is sometimes called Scheele's process. N. Lemery (1675) and J. C. Barchusen (1703) believed that the difference in the two mercury chlorides is due to the corrosive sublimate having united with more acid than is the case with calomel; and later, after the discovery of chlorine, the difference in the composition of the two salts was made clear. R. Chenevix first analyzed the two chlorides in 1802.

In 1776, P. Woulfe [2] discovered at Zweibrücken (Rhine Palatinate) a mineral,

horn mercury or *horn quicksilver*, to which M. Sage applied the term *mine de mercure cornée*, and concerning which J. B. L. Romé de l'Isle said: "*Mine de mercure cornée volatile*, or *mercure doux natif*, is mercury solidified and mineralized by muriatic acid . . . it appears to have been sublimed on the walls of the cavities in certain mines." At first, P. Woulfe, and R. Kirwan thought that horn mercury contains some sulphate, but R. J. Haüy regarded it as *le muriate de mercure des chimistes*. Horn mercury was shown by J. L. Proust, L. Gmelin, and C. F. Rammelsberg to be identical with mercurous chloride. The mineral is comparatively rare; it occurs in translucent tetragonal crystals as a secondary mineral. Specimens have been reported from the Palatinate, Lüneberg, and Giftberg (Germany); Idria (Carniola); Avala (Serbia); Almaden (Spain); Montpellier (France); El Doctor (Mexico); Terlingua (Texas); Sarawak (Borneo), etc.

The preparation of mercurous chloride.—1. *By the action of chlorine or hydrogen chloride on mercury.*—R. Cowper[3] found that chlorine attacks mercury energetically no matter whether the gas be moist or thoroughly dried, although W. A. Shenstone and C. R. Beck found the action is much slower when the gas is highly purified, and dry mercury burns with an orange flame when heated in chlorine gas, forming a mixture of mercury chlorides; at ordinary temp., C. E. Schafhäutl, and I. Bhaduri found mercurous chloride is formed if the metal be in excess, and similar remarks apply to the action of chlorine water. M. Berthelot said that in the presence of air, hydrogen chloride and mercury form mercurous chloride. He also stated that hydrogen chloride does not attack mercury in the cold, but in the presence of a little oxygen, mercurous chloride together with a little oxychloride are slowly formed; the speed of the reaction is favoured by moisture and the presence of alkali chlorides. G. H. Bailey and G. J. Fowler said that the oxychloride $Hg_2OCl_2.H_2O$ is formed in the reaction which "proceeds in the dark as well as when exposed to light, and indeed powerful sunlight seems, if anything, unfavourable to it." M. Berthelot added that hydrogen chloride does not attack mercury at 200°; but if mercury be electrified in the presence of hydrogen chloride, hydrogen and mercurous chloride are formed.

C. E. Schafhäutl, and P. Süss say that mercury slowly reduces an aq. soln. of ferric chloride, and rapidly if the soln. be acidified with hydrochloric acid: $FeCl_3+Hg=HgCl+FeCl_2$; and C. E. Schafhäutl studied the old process for preparing mercurous chloride by sublimation from an intimate mixture obtained by triturating mercury with sodium chloride, ferric sulphate or basic ferric sulphate and water, some ferric chloride is probably sublimed with the mercurous chloride: $Fe_2(SO_4)_3+6NaCl+2Hg=3Na_2SO_4+2FeCl_2+2HgCl$. P. L. Geiger recommended making mercurous chloride, by triturating two gram-atoms of mercury with two mols of sodium chloride, and one of manganese dioxide, and heating the mixture with two mols of sulphuric acid until the mercurous chloride sublimed: $2Hg+2NaCl+MnO_2+2SO_3=Na_2SO_4+MnSO_4+2HgCl$. O. Henry, and J. Raab sublimed a mixture of mercury, mercuric sulphate, and salt: $HgSO_4+Hg+2NaCl=2HgCl+Na_2SO_4$; or $HgSO_4+Hg=Hg_2SO_4$; and $Hg_2SO_4+2NaCl=Na_2SO_4+2HgCl$.

2. *By the action of chlorides on mercurous salts.*—As shown by C. W. Scheele (1778), mercurous chloride is precipitated when an aq. soln. of a mercurous salt is treated with sodium chloride, and the precipitate washed with cold water. The mercurous chloride so obtained is a fine powder. J. A. Buchner, and L. Mailhe found that when mercurous nitrate is used, the precipitate is contaminated with basic mercurous and mercuric nitrates; but not if the mercurous nitrate be very dil., and the sodium chloride be added in excess, and the liquid be warmed with the precipitate for some time. With the same object, N. G. Sefström, P. L. Geiger, and J. B. Trautwein recommended using a soln. of mercurous nitrate acidified with nitric acid; and R. Chenevix, a soln. of sodium chloride acidified with hydrochloric acid. E. Schmidt's directions are:

A soln. of 10 parts of mercurous nitrate, 1·5 parts of nitric acid, and 88·5 parts of water is poured with constant stirring into a clear soln. of 3 parts of sodium chloride in 12 to 15

parts by weight of water. To avoid the formation of sparingly soluble basic mercurous nitrates, the sodium chloride is kept in excess by pouring the mercurous nitrate soln. into that of sodium chloride, not conversely. The precipitated mercurous chloride is allowed to settle away from light and the supernatant liquor poured off; it is stirred up with cold water, and the operation repeated until the wash liquor gives no turbidity with silver nitrate. The precipitate is collected on a filter and dried.

According to J. B. A. Dumas, the precipitate cannot be freed from sodium chloride by washing, and he says this explains why the precipitated salt is more soluble than the sublimed; but L. Mailhe said that only a small trace of sodium chloride is retained by the precipitate, and the solubilities of the sublimed and precipitated salts are the same. The precipitated salt in the finer state of subdivision may dissolve more quickly than the sublimed salt. T. Martius recommended using ammonium chloride in place of sodium chloride, but there is then a difficulty in removing the ammonia from the precipitate, and F. J. Otto does not recommend the process, although M. Fleischmann says that the whole of the ammonia can be removed from the precipitate by a prolonged washing with cold water. N. J. B. G. Guibourt precipitates mercurous chloride by adding hydrochloric acid to a conc. soln. of a mercurous salt; L. Gmelin says that heating should be avoided, and that a dil. soln. gives better results. R. Varet recommends precipitating with a soln. of potassium chloride, and, after washing, drying in darkness at 110°. W. Sievers passed chlorine into a feebly acid conc. soln. of mercurous nitrate and washed the mixture of mercurous and mercuric chlorides with hot water to remove the mercuric chloride. The precipitate was dissolved for a long time with a boiling soln. of mercurous nitrate; and the crystals which separated from the cooling soln. were washed first with nitric acid, and then with water. H. Debray first showed that lustrous crystals are deposited from a soln. of calomel in one of hot mercurous nitrate. Mercurous chloride is also formed, when mercurous oxide is treated with hydrochloric acid. L. A. Planché prepared mercurous chloride by sublimation from an intimate mixture of mercurous sulphate and sodium chloride. The directions in the British Pharmacopœia are:

> Moisten 10 parts of mercuric sulphate with some water and rub it with 7 parts of mercury until globules are no longer visible; add 5 parts of sodium chloride and thoroughly mix the whole by continued trituration. When dry, sublime in a suitable apparatus into a chamber of such a size that the calomel, instead of adhering to its sides as a crystalline crust, shall fall as a fine dull white powder on its floor. Wash this powder with boiling distilled water until the washings cease to be darkened with ammonium sulphide. Finally, dry at a heat not exceeding 100°, and preserve in a jar or bottle impervious to light.

Sublimed calomel condenses as a dense fibrous mass which requires pulverization before use; as in the manufacturing process when, for medical purposes, the calomel is required in a fine state of subdivision. E. Soubeiran and F. C. Calvert recommended carrying the vapour of the subliming calomel by means of a stream of cold air, into a large chamber where the salt was condensed. J. Jewel, and O. Henry proposed a stream of steam instead of air. G. Lunge and E. Divers have described how calomel—*keifun*—free from corrosive sublimate is made in Japan:

> Balls of porous earth and salt—from the bittern of partially evaporated sea-water—are heated along with mercury in iron pots with earth. The magnesium salts derived from the bittern, together with the air which diffuses into the pots, form hydrogen chloride, and this reacts with the mercury which sublimes into the clay covers of the pots: $4Hg+4HCl+O_2=4HgCl+2H_2O$, so that the covers become filled with a network of micaceous scales of white or pale cream-coloured calomel.

3. *By the reduction of mercuric chloride.*—As known to the alchemists, mercurous chloride can be prepared by the reduction of mercuric chloride, say, by triturating it with mercury, and heating the mixture until it sublimes. A great deal of the mercuric chloride is reduced during the trituration. J. B. Trautwein warmed the mixture for some hours and again triturated it before sublimation.

> On a large scale, 17 parts of corrosive sublimate are mixed with a little alcohol or water, and rubbed up with 13 parts of mercury until the metal is "deadened." The mixture is

then sublimed in glass flasks. The calomel condenses in the upper cooler part of the flask as a solid, translucent, fibrous cake. The flasks are broken, and the cake removed. The cake is ground to powder and washed repeatedly with boiling water.

G. F. Hildebrandt said that the alchemists used to repeat the sublimation a number of times, for they refer to calomel six or seven times re-sublimed, and to *panacea mercuralis* re-sublimed nine times.

F. Wöhler reduced mercuric to mercurous chloride, by digesting a sat. aq. soln. of mercuric chloride and *sulphur dioxide* at 50° for some time, and washing the precipitated mercurous chloride. According to A. Vogel, the reduction is complete only with a large excess of sulphur dioxide frequently renewed. J. Zinkeisen, and F. Muck employed a sat. soln. of mercuric chloride above 75°, below this temp. the reaction is not complete. W. Stein, and F. Sartorius emphasized the use of dil. mercuric chloride soln. (say, 1 : 80) at 70° to 80° under which conditions the reduction is almost quantitative; indeed, D. Vitali employed the reaction for the determination of mercuric chloride. R. Wagner recommended treating an alcoholic soln. of mercuric chloride with sulphur dioxide. H. Rose treated the mercuric chloride soln. with boiling *ammonium sulphite* (if cold, there is no appreciable reduction, and if the boiling be prolonged, P. Berthier says the calomel is partly reduced to mercury); J. Meyer recommended warm *lithium sulphite*; H. Rose reduced mercuric chloride soln. with *hypophosphorous acid* (when the mercuric chloride is in excess, otherwise mercury is precipitated); and C. Glücksmann used an excess of *barium hypophosphite* in the presence of hydrochloric acid, and found the reaction quantitative; W. Hempel reduced mercuric chloride with *ferrous sulphate;* T. Fairley, with *hypochlorites;* N. A. E. Millon, with *potassium hydrogen oxalate;* and J. Schoras, and W. Uloth, with *oxalic acid.* J. M. Eder exposed a mixture of mercuric chloride and oxalic acid to sunlight; P. A. von Bonsdorff reduced mercuric chloride with *formic acid;* F. W. O. de Coninck and M. Dautry, with *malonic acid;* and P. Duret with *dextrose.* The last-named claimed by the following process to prepare a fine-grained, light, and voluminous form of calomel with greater germicidal powers than the ordinary preparations when used in prophylactic ointments, or anti-syphilitic injections:

A soln. containing 5 grms. of sodium hydrogen carbonate and 10 grms. of dextrose in 80 c.c. of water is added to a soln. containing 7·5 grms. of crystalline magnesium chloride in 20 c.c. of water, and this mixture is added to a soln. containing 11·5 grms. of mercuric chloride and ten drops of hydrochloric acid in 100 c.c. of water in a flask. When the reaction has ceased, the mixture is heated on a water-bath until all the carbon dioxide is evolved. The finely divided precipitate of mercurous chloride is then collected and washed with water.

M. Gambier claimed to have made still more active calomel by varying the precipitating and reducing agents.

J. H. Gladstone and A. Tribe reduced mercuric chloride by dipping a plate of platinum or gold in a soln. of mercuric chloride, and connecting it electrically with mercury, also in contact with the same soln. F. Paschen, and A. W. Laubengayer, noted the formation of mercurous chloride at the surface of a mercury anode in hydrochloric acid, etc.

When a sample of dry mercurous chloride is heated in a test-tube it should volatilize completely without giving off acid fumes. If the calomel were adulterated with powdered barytes, etc., this would remain as a non-volatile residue; and if mercurous or mercuric nitrate were present, fumes of nitrogen peroxide would be evolved. Adulterations with gum or other organic matters are detected by the smell when heated. The aq. extract of the salt when filtered and evaporated to dryness should give no residue showing the absence of soluble salts, and the aq. extract should not give a white turbidity with stannic chloride soln. showing the absence of mercuric chloride. E. F. Anthon recommended extracting with ether or alcohol. According to H. Bonnewyn, if a clean knife-blade be immersed in the calomel moistened with alcohol or water, a black spot may be formed on the blade

if as little as 2×10^{-5} parts of mercuric chloride be present. Mercury may be detected by the miscrocope, or by shaking the calomel with nitric acid diluted with its own vol. of water when any metallic mercury will be dissolved. The filtrate is then tested for mercury by hydrogen sulphide, etc.

A. Lottermoser [4] found that if chlorine water be added to a soln. of colloidal mercury, the liquid becomes milky or turbid and **colloidal mercurous chloride** is formed—if an excess be added, colloidal mercuric chloride is formed. E. von Meyer and A. Lottermoser also added a soln. of mercuric chloride to colloidal silver and obtained a milky hydrosol of mercurous chloride. A. Gutbier also prepared the same hydrosol by adding hydroxylamine hydrochloride to a soln. of a mercurous salt, or hydrazine hydrate to a very dil. soln. of mercuric chloride. The Chemische Fabrik von Heyden patented the following process :

> Dissolve 100 parts of sodium lysalbinate in 4000 parts of water, and add a soln. of 40 parts of sodium chloride in 2000 parts of water, and then a soln. of 120 parts of mercurous nitrate in 4000 parts of water. When an acid is added, the precipitate which is obtained can be washed with water. The precipitate is soluble in a very dil. soln. of alkali, and the soln. can be evaporated to dryness.

The white solid forms a milky fluid with water 1 : 50 ; it is insoluble in alcohol, ether, benzene, and chloroform. H. Lachs studied the scintillation of mercurous chloride as an ultramicroscopic colloid, and found that the effect diminishes with long standing owing to the development of long crystals.

The properties of mercurous chloride.—The **crystals** of the natural product occur in bipyramids belonging to the tetragonal system with the axial ratio, according to J. Schabus,[5] $a : c = 1 : 1{\cdot}7356$; W. F. Hillebrand and W. T. Schaller give $a : c = 1 : 1{\cdot}7232$. The product obtained by sublimation is a compact crystalline mass unless precautions are taken to keep the product pulverulent—the Japanese product is in micaceous crystals. The precipitated salt is usually a white powder. A soln. of mercurous chloride in a hot soln. of mercurous nitrate, as indicated previously, gives crystals with a mother-of-pearl lustre. H. Behrens obtained needle-like crystals from a soln. of mercurous nitrate and hydrochloric acid. E. Mitscherlich, and W. J. Luczizky obtained from ethyl and methyl alcohol soln. rhombic crystals with axial ratios $a : b : c = 0{\cdot}7251 : 1 : 1{\cdot}069$; and the latter also obtained a second rhombic form, so that this compound appears to crystallize in three different forms—see mercuric bromide. The **specific gravity** of native mercurous chloride by W. Haidinger [6] is 6·482 ; and the reported numbers for artificial crystals vary from the 6·56 of H. Schiff to the 7·178 of L. Playfair and J. P. Joule. According to J. Meyer, the lustrous scales prepared from mercuric chloride and lithium sulphite have a sp. gr. 4·5 to 5·0, but show no difference of potential against ordinary mercurous chloride in a galvanic cell, and in consequence do not appear to be an allotropic modification of the latter. A. Reis and L. Zimmermann gave 2·6 for the **hardness**.

The **specific heat** of mercurous chloride, measured by A. Magnus [7] between 15° and 100° is 0·05296 ; and the **molecular heat,** $12{\cdot}48 \pm 0{\cdot}065$. H. V. Regnault gives 0·05205 for the sp. ht. A. Eucken showed that the mol. heat decreases as the temp. is reduced, being 11·43 at 17·5° ; 10·70 at −67·5° ; and 9·46 at −168·2° ; and, according to F. Pollitzer, the mol. ht. of crystalline mercurous chloride falls from 11·51 at −74° to 8·44 at −199·5° ; and, for the pulverulent salt, from 9·03 at −184° to 8·79 at −190°. E. Jannetaz gives 0·77 for the square root of the ratio of the **heat conductivities** of mercurous chloride crystals in the direction of the chief axis and in the direction of the base. T. Carnelley gives for the **melting point** 302°, but, as W. Hampe showed, in open vessels, it vaporizes without melting. M. Faraday obtained no signs of vaporization at ordinary temp., but C. Zenghelis placed mercurous chloride 5 cms. above a silver plate for a month, and found that the silver was attacked—presumably by the vapour of the calomel. H. Arctowsky heated calomel to different temp. for 5 hrs. and measured the loss of weight ; he found at 86·5° a loss of 0·005 grm. ; at 98·5°, 0·0013 grm. ; at 120·25°, 0·0025 grm. ;

at 152°, 0·014 grm.; and at 175·25°, 0·058 grm. M. Berthelot noted a perceptible volatilization at 250°. W. P. A. Jonker gives the **sublimation point** as 373°; A. Smith and A. W. C. Menzies say the **boiling point** at atm. press. is 382·5; A. Smith and R. P. Calvert, 383·7°; W. P. A. Jonker, 373°; and W. Harris and V. Meyer give 357°. J. C. G. de Marignac gives the **latent heat of vaporization** per gram 131 cals. at 16°; 127 cals. at 18°. A. Smith and R. P. Calvert found that the **entropy of vaporization** of mercurous chloride corresponds with the value for associated liquids; by Trouton's rule, 18·7; and by Hildebrand's rule, 17·7 for a conc. 0·005 mol per litre.

The **vapour pressure** of mercurous chloride in equilibrium with the solid below 180° was determined by E. Wiedemann, K. Stelzner, and G. Niederschulte, and by A. Smith and A. W. C. Menzies for temp. exceeding 360°. The vapour press. p mm. of mercury at $\theta°$ is:

θ	90°	110°	150°	170°	180°	360°	370°	380°	390°	400°
p	0·004	0·011	0·07	0·27	0·45	434	556	712	906	1135

The salt carefully dried over phosphorus pentoxide gives no appreciable vap. press. after being held for 15 mins. at 352°.

Determinations of the **vapour density** of mercurous chloride by E. Mitscherlich,[8] H. St. C. Deville and L. Troost, and R. Rieth show but half the value calculated for Hg_2Cl_2. For example, the vapour density of mercuric chloride at 518° is 235·5 (O_2=32). This number agrees with 235·5 required for the simple mol. HgCl. If mercury be a dyad, and if it has a constant unchangeable valency, the formula should be Hg_2Cl_2, that is, Cl—Hg—Hg—Cl. In that case, the observed vapour density means that the mercurous chloride dissociates into mercuric chloride and mercury: $Hg_2Cl_2=Hg+HgCl_2$, the theoretical vapour density of which is $\frac{1}{2}(200+270·9)=235·5$, the same as for HgCl. The vapour density determination does not therefore furnish a definite answer to the obvious question.

W. Odling showed that calomel vapour amalgamates gold-leaf, and hence inferred that probably some mercury is present. J. C. G. de Marignac also deduced from the latent heat of vaporization that *s'il y a commencement de dissociation, il est au moins extrêmement limité*. H. Debray could find no amalgamation at 400°, but H. B. Baker obtained it at 445°. E. Erlenmeyer obtained a very small proportion of free mercury in a deposit of sublimed calomel; and H. Debray obtained free mercury by rapidly cooling the vapour by a gilded silver tube cooled by running water. All these experiments show that probably free mercury vapour is present in calomel vapour, although it might be argued that gold-leaf decomposes the vapour of calomel. At best, the preceding experiments show that some dissociation occurs, whereas the observed vapour density requires almost complete dissociation. The argument based on the constant valency of mercury is of no value. H. B. Baker claimed that the vapour density of calomel, perfectly dry, corresponds with the formula Hg_2Cl_2 as shown (*a*) by the vapour density, and (*b*) by the absence of the amalgamation with gold, but if the calomel be not so completely dried, it is probable that Hg_2Cl_2 dissociates into Hg and $HgCl_2$, analogous with the behaviour of perfectly dried ammonium chloride, which is known to behave in this manner. H. Debray argued that the decomposition cannot be complete because the condensation of the vapour yields mercurous and mercuric chlorides as well as mercury. According to W. Harris and V. Meyer, gold-leaf is amalgamated at the moment when it is inserted in the calomel vapour, but on becoming hot, the gold amalgam is dissociated and the colour of the gold is restored. W. Harris and V. Meyer attempted to determine the amount of dissociation. They heated calomel to 465° in a wide glass tube containing a narrower porous vessel. They obtained a "dense mass" of mercury (with the heavier vapour) in the wider tube, and a "considerable amount" of corrosive sublimate in the inner cell, and hence said that this result proves a copious dissociation of the calomel vapour. The conclusion is a *non sequitur* because the removal of a small proportion of one product of dissociation

would disturb the equilibrium, and in accord with the law of mass action would liberate far more mercury than would be represented by the actual amount of dissociation in the undisturbed vapour. W. Harris and V. Meyer then assumed that a vapour largely composed of mercurous chloride should give the reactions of a mercurous salt while one composed largely of mercury and mercuric chloride should give the reactions of a mercuric salt. They show that a rod of solid potassium hydroxide at 240°–260°, when immersed in the vapour of calomel in another tube at the same temp., is immediately covered with a layer of red mercuric oxide just as occurs with the vapour of mercuric chloride, and although mercurous oxide is unstable at this temp., W. Harris and V. Meyer assumed that their experiment would have shown its presence as a transient intermediate compound if mercurous chloride vapour had been present. They also say that the mercuric oxide was not formed by the decomposition of the mercurous oxide, because a stick of potash coated with mercurous oxide forms no perceptible mercuric oxide in 15–25 secs. The conclusion that the mercuric oxide could not have arisen from previously formed mercurous oxide, but is a direct product of the interaction with the vapour from calomel is probably correct, because there is no particular reason for assuming that mercurous oxide would be formed under these conditions if the vapour really contained mols. of mercurous chloride. There is no justification in these results for the sweeping conclusion that "calomel vapour decomposes completely according to the equation: $Hg_2Cl_2=HgCl_2+Hg$." In a controversy with V. Meyer, M. Fileti claimed that the vapour density of calomel in the presence of the vapour of mercuric chloride corresponds to HgCl, not Hg_2Cl_2, and that there is no dissociation because gold-leaf (cooled by water) is not amalgamated. In fine, none of these qualitative experiments can give a quantitative idea of the proportion of dissociated—$Hg+HgCl_2$—to undissociated—HgCl—mols. in calomel vapour.

A. Smith and A. W. C. Menzies calculated the vap. press. of calomel on the extreme assumptions that there is no dissociation, and that there is complete dissociation. The vap. press. of a mixture of calomel and mercury will be equal to the sum of the vap. press. of mercury and calomel, if there be no dissociation, and less than this sum if dissociation of the calomel vapour occurs. Experiment showed that the observed vap. press. of the mixture is less than that calculated for complete dissociation. This was traced to a slight lowering of the vap. press. of mercury owing to its dissolving a little calomel. Allowing for this, A. Smith and A. W. C. Menzies' measurements give numbers in close agreement with the view that the vapour of calomel is completely dissociated, and that mols. of the types HgCl and Hg_2Cl_2 are not present in the sat. vapour of calomel.

A. Smith and R. P. Calvert have determined the **dissociation pressures** of calomel vapour and find at 309·52°, the dissociation press. is 103 mm.; at 341·56°, 261·4 mm.; at 367·72°, 522·5 mm.; and at 383·95°, 764·7 mm. If p denotes the press. in mm. of mercury at the absolute temp. $T°$, the observed results can be very well represented by the formula: $\log p=-7792{\cdot}10T^{-1}-12{\cdot}2309 \log T+49{\cdot}2048$. According to A. Smith and A. W. C. Menzies, the lowering of the vap. press. of mercury by the soln. of calomel between 360° and 400° corresponds with the **molecular formula** HgCl; and, according to E. Beckmann, the lowering of the f.p. of mercuric chloride by the soln. of mercurous chloride agrees with the formula Hg_2Cl_2.

T. Andrews [9] first measured the heat disengaged during the combination of mercury with chlorine, and he says, "The primary compound formed in this reaction is probably $HgCl_2$, but by the action of the excess of mercury a portion is afterwards converted into the subchloride Hg_2Cl_2." According to R. Varet, the **heat of formation** of mercurous chloride from liquid mercury and chlorine gas is $(2Hg, Cl_2)$ =62·65 Cals. W. Nernst gives 62·6 Cals.; J. Thomsen, 62·55 Cals. According to M. de K. Thompson, the **free energy of formation** at 18°, with chlorine at atm. press., is −49·4 Cals., or with respect to liquid chlorine, −50·0 Cals., or calculated from the solubility of mercurous chloride, −52·1 Cals.; and the **total energy** is

between −57·6 and 62·0 Cals. J. Thomsen gives for $Hg_2(NO_3)_{2aq.}+2KCl_{aq.}=24·32$ Cals.; and for $Hg_2O+2HCl_{gas}=64·71$ Cals. M. Berthelot gives for the $Hg_2Cl_2=HgCl_{2solid}+Hg_{liquid}$ −19 Cals. R. H. Gerke gave for the entropy change at 25°, $Hg+\frac{1}{2}Cl_2=HgCl$ −21·8.

The crystals have a positive double refraction, and A. des Cloizeaux[10] says the **indices of refraction** for the red ray are $\omega=1·96$, and $\epsilon=2·60$; while H. Dufet gives for the Li-line, $\omega=1·9556$, and $\epsilon=2·6006$; for the Na-line, $\omega=1·97325$, and $\epsilon=2·6559$; and for the Tl-line, $\omega=1·99085$, and $\epsilon=2·7129$. W. Haidinger says the sublimed crystals from Schmölnitz are pleochroic, for the ω-ray is pale wine yellow and the ϵ-ray reddish-brown. J. A. Wilkinson says the crystals have an orange fluorescence, and O. Wolff that they exhibit an orange **luminescence** in ultra-violet light, but no thermo-luminescence. A. L. Hughes has shown that mercurous chloride gives a well-marked **photoelectric effect.** E. J. Evans studied the **absorption spectrum** of mercurous chloride vapour.

According to V. von Lang,[11] mercurous chloride is diamagnetic. C. Fritsch found the **electrical conductivity** of a plate of pressed powder increases from 31 to 130 mhos when mixed with 1 per cent. of sodium chloride, and to 1700 with 2 per cent. of sodium chloride. W. Hampe says the molten salt conducts electrolytically. E. Rothe gives the **electromotive force** of the calomel electrode as 0·56 volt. R. Behrend found the e.m.f. of the cell Hg | HgCl, $\frac{1}{10}N$-KCl | $\frac{1}{10}N$-$HgNO_3$, HNO_3 | Hg to be 0·391 volt; A. Ogg for the same cell with N-HNO_3 and N-KCl found 0·466 volt; H. Ley and C. Heimbucher, for the cell Hg | HgCl, $\frac{1}{10}N$-KCl | $\frac{1}{10}N$-$HgClO_4$ | Hg, 0·420 volt (20°); and for the same cell with $\frac{1}{100}N$-KCl, 0·472 volt. The conc. of the ions $Hg_2^{\cdot\cdot}$ in the sat. calomel soln. calculated from the e.m.f. of these cells are respectively $1·6\times10^{-6}$; $1·0\times10^{-6}$; $0·72\times10^{-6}$; and $0·79\times10^{-6}$. L. S. Bagster and B. D. Steele gave for the cell Hg | HgCl, $SO_{2liquid}$ | SO_2 | $PbCl_2$, $SO_{2liquid}$ | Pb, 0·43 volt. R. Luther also showed that the grain-size of the calomel exercises an important influence on the e.m.f. A. W. Laubengayer has shown that the apparent polarization of the calomel electrode is probably due to the formation on the surface of the mercury anode, of a strongly adsorbed film of mercurous chloride which offers a high resistance to the passage of the current. The calomel cell has been studied by H. A. Fales and W. A. Mudge, S. Bodforss, etc. W. R. Hainsworth and D. A. MacInnes measured the effect of press., p, up to 400 atm. on the cell H_2 | HCl(0·1N), HgCl—Hg at 25°, and found for the change of e.m.f. $dE=0·02958\ \log\ p+6·56\times10^{-6}(p-1)+3·7\times10^{-10}(p^2-1)$. R. H. Gerke studied the e.m.f. of the cell Hg | HgCl, N-HCl | Cl_2 at atm. press. B. H. Buttle and J. T. Hewitt give the **ionization constant** $HgCl^{\cdot}=Hg^{\cdot\cdot}+Cl'$ as $5·3\times10^{-8}$.

Mercurous chloride has no smell and no taste. Calomel is not altered when exposed to air in darkness, but in *light*, according to G. Suckow,[12] calomel acquires superficially a grey tint. R. Abegg found that it is also coloured by exposure to the cathode rays. L. Gmelin suggested that the grey product is *mercurous sub-chloride*, Hg_4Cl_2; but the action is probably a decomposition of the calomel into mercuric chloride and mercury, $2HgCl=Hg+HgCl_2$. Thus, J. von Tugolessoff says:

> Sheets of paper were soaked in a soln. of mercurous nitrate, dipped in a dil. soln. of hydrochloric acid, dried, and exposed under a negative plate to light. The action of the light was to be detected by means of the mercuramide compounds. Since those of the mercurous salt are black and those of the mercuric salt are white, it was expected that ammonia would only blacken the parts which had not been exposed to light. The experiment did not turn out at first as had been hoped, for the whole sheet of paper was blackened by ammonia. After a short treatment with very dil. hydrochloric acid, the high lights became white. This shows that mercurous chloride is unquestionably changed to mercuric salt by light, but not completely; and consequently the test was spoiled by the ammonia reacting with some of the undecomposed mercurous salt. Since the amount of this latter was not large, a very short exposure to acid was sufficient to remove it, while the acid had practically no more effect on the portions which had not been exposed to light.

Calomel is blackened when exposed to light while confined under water, and A. Vogel

could find no sign of the evolution of any gas during the change. According to A. Mailfert, *ozone* acts slowly on mercurous chloride, forming mercuric chloride and a brick-red precipitate, apparently an oxychloride.

Mercurous chloride is very sparingly soluble in water. According to F. Kohlrausch,[13] a litre of water dissolves 0·002 grm. of mercurous chloride at 18° or 0·0014 grm. at 0·5°; 0·0021 grm. at 18°; 0·0028 grm. at 24·6°; and 0·0070 grm. at 43°. Several other data have been calculated from the electrical conductivity or from the electromotive force of galvanic cells by H. Ley and C. Heimbucher, A. Ogg, R. Behrend, L. Rolla, M. S. Sherrill, M. de K. Thompson, etc. L. Sauer found that the finely divided salt is 10 per cent. more soluble than coarse-grained.

There have been many discrepant statements as to the conversion of mercurous into mercuric chloride by water, the chlorides of the alkali metals, and by organic acids. P. Hoglan [14] found that calomel is slowly converted into corrosive sublimate by water at the temp. of the body and that the presence of sodium chloride, citric acid, or sugar favours the conversion. Some discrepant statements are due to a comparison of results obtained at different temp., at low temp. the conversion is slow, while at body temp. calomel is an unstable compound. M. Berthé says the conversion of mercurous to mercuric chloride by water or alcohol occurs at least at 40° or 50°. S. Hada found when freshly precipitated mercurous chloride is heated with water for 7 hrs. in a flask immersed in boiling water, mercury collects as a sublimate and mercuric chloride is found in the soln. The results with a current of air and a current of carbon dioxide were virtually the same; about one-tenth of a gram of mercury was present as mercuric chloride per gram of mercurous chloride employed, the amount of mercuric chloride was augmented to 0·13 grm. by the presence of hydrochloric acid, and nearly doubled by the presence of alkali chloride. According to G. Righini, steam partially converts calomel into a grey product with an excess of mercury and mercuric chloride; similar remarks apply to the action of boiling water. According to M. Donovan, N. J. B. G. Guibourt, W. Gruner, and A. Vogel, the grey product is a basic mercurous chloride, because (i) it recovers its whiteness when boiled with hydrochloric acid; (ii) when sublimed it yields mercurous chloride and mercury; and (iii) the water contains a little hydrochloric acid, and mercuric chloride. S. Hada found that if shaded from light, there is no sign of the grey product or of any oxidation of the mercury by hydrolytic dissociation, for mercurous chloride may be boiled indefinitely with water without suffering any change in appearance or composition. Indeed, according to W. Gruner and J. F. Simon, the calomel "almost wholly disappears after six boilings," when with water frequently replaced, and the water contains mercuric chloride; and, according to L. Mailhe, and S. Hada, the conversion of mercurous into mercuric chloride is faster if air has access to the liquid. In his study: *How mercurous and mercuric salts change into each other*, S. Hada could find no evidence of any oxidation during the decomposition of mercurous into mercuric chloride under these conditions, and he says dissociation fully accounts for all the facts observed. He finds that calomel is scarcely altered when heated for 6 hrs. to 150° with water in a sealed tube in an atm. of carbon dioxide—dissociation is hindered by the retention of the mercury vapour; although more dissociation occurs if hydrochloric acid or potassium chloride be present than with water alone. If the atm. in the tube contains oxygen, the mercury is oxidized—part of the oxychloride remains in soln. and part separates as brown glistening micaceous scales.

Two **mercurous oxychlorides** occur in small quantities in nature as secondary minerals, derivatives of cinnabar; the one, *eglestonite*, $Hg_2O.2HgCl$, occurs in brown crystals belonging to the cubic system along with mercury and mercuric sulphide at Terlingua (Texas).[15] The sp. gr. is 8·327; hardness, 2 to 3. A. J. Moses' and B. F. Hill's analyses gave $Hg_6O_2Cl_3$, but W. F. Hillebrand and W. T. Schaller's is that generally accepted—Hg_4OCl_2. The other mercurous oxychloride is *terlinguaite*, which occurs at Terlingua (Texas) in sulphur-yellow needles or plates belonging to the monoclinic system, with axial ratios $a : b : c = 1·6050 : 1 : 2·0245$,

and $\beta=105° 37'$; sp. gr. 8·723 to 8·728; and hardness, 2 to 3. W. F. Hillebrand and W. T. Schaller's analyses agree with the formula HgO.HgCl, so that it is a kind of mercuric mercuroxychloride. The colour gradually changes to an olive-green on exposure to sunlight. T. Fischer and H. von Wartenburg prepared artificial crystals of terlinguaite by heating a mixture of equi-mol. parts of mercuric oxide and mercurous chloride with water in a sealed tube at 180°.

According to H. Moissan,[16] when mercurous chloride is warmed in the presence of *fluorine*, it furnishes a yellow surface skin of a compound insoluble in water; *chlorine* gas or chlorine water converts mercurous into mercuric chloride—according to M. Berthelot, $(Hg_2Cl_2, Cl_{2aq.})=32·6$ to 45·6 Cals., and, according to J. Thomsen, 37·075 Cals. W. Eidmann and A. Naumann report that when chlorine is passed into acetone with mercurous chloride in suspension, only a small proportion of the latter is converted into the mercuric salt; *bromine* acts rapidly: $2HgCl+Br_2=HgCl_2+HgBr_2$; and with iodine: $2HgCl+I_2=HgCl_2+HgI_2$, and the sparingly soluble mercuric iodide is precipitated. A. Potilitzin found that bromine displaces some of the chlorine in mercurous chloride; M. C. Schuyten found that both bromine and iodine oxidize mercurous chloride; L. A. Planché and E. Soubeiran found that by triturating mercurous chloride with water and iodine both mercuric chloride and iodide are formed; and E. Riegel and F. Selmi prepared what he regarded as yellow crystals of **mercuric chloroiodide,** $2HgCl_2.HgI_2$, by heating mercurous chloride with iodine and much water until iodine vapour is no longer evolved—the yellow crystals which are deposited from the soln. become yellow in a few days. The mother liquid, according to F. Selmi, contains some mercurous chloride, chlorate, and iodate, and hydrochloric acid.

Mercurous chloride is very sparingly soluble in *hydrochloric acid*. E. Ruyssen and E. Varenne[17] have measured the solubility of mercurous chloride in different amounts of hydrochloric acid, and they express the solubility as a ratio between the weight of mercurous chloride dissolved and the weight of acid—the solubility increases as the proportion of acid increases. At first the rate of dissolution is slow, but after several days, the rate of solution increases rapidly. Mercurous chloride is more soluble in the presence of silver chloride than when alone. The action of hydrogen sulphide on a hydrochloric acid soln. of mercurous chloride gives a precipitate ranging in colour from bright yellow to orange-yellow, according to the relative proportions of mercurous and mercuric chlorides in the soln. Expressing the results in grams of mercuric chloride per litre, T. W. Richards and E. H. Archibald found for the effect of hydrochloric acid on the solubility of mercurous chloride:

HCl .	31·69	95·43	158·4	209·2	267·3	278·7	317·3	264·6
$HgCl_2$.	0·034	0·207	0·399	0·548	0·654	0·675	0·670	0·673
Sp. gr. .	—	0·042	1·069	1·091	1·114	1·119	1·132	1·153

N. J. B. G. Guibourt found that boiling water acidulated with hydrochloric acid dissolves mercurous chloride as mercuric chloride without the separation of mercury if air has access to the liquid, and L. Mailhe says that less is dissolved if the air be excluded. Thus, between 40° and 50°, 100 parts of calomel in a stoppered bottle with 100 parts of hydrochloric acid and 1667 parts of water, thoroughly freed from air by boiling, take up 0·67 part of mercuric chloride in 24 hrs., while in an open vessel, 2·32 parts were taken up. L. J. Proust, and P. F. G. Boullay say that boiling hydrochloric acid decomposes mercurous chloride, forming mercuric chloride and mercury; and, according to M. Berthelot, **mercuric hydrochloride,** $HgCl_2.n$HCl, is the product of the action. M. Pettenkofer, C. H. Pfaff, and H. Hennell found that when a mixture of ammonium chloride and calomel is sublimed, the sublimate is a double ammonium mercuric chloride, and a similar action is supposed to occur when calomel is boiled with an aq. soln. of ammonium chloride. In subliming a mixture of sodium and mercurous chloride, the latter is not decomposed. Like hydrochloric acid, aq. soln. of the chlorides of sodium, barium, calcium, etc.,

in contact with mercurous chloride form mercury and mercuric chloride. L. Mailhe, A. Larocque, J. Gewecke, and J. F. Simon reported that soln. of ammonium chloride take up mercuric chloride from mercurous chloride at ordinary temp., the action being faster between 40° and 50°; and faster with conc. than with dil. soln.; and faster in the presence of air than in its absence. On the other hand, T. Martius, and P. H. le Page say that dil. soln. of ammonium chloride have no such action. Alkali and other metal chlorides behave like ammonium chloride, but the action is less pronounced. The reaction seems to have been noticed by J. Capellina in 1576 before L. J. Proust's study in 1815; H. Pick said that mercurous chloride is blackened by a soln. of potassium chloride. *Au contraire*, A. Larocque said that soln. of the alkali chlorides dissolve the calomel as calomel without changing it simultaneously to mercuric chloride, because when the soln. is agitated with ether no mercuric chloride is extracted by this solvent. The action takes place in darkness. T. W. Richards and E. H. Archibald say the action is more marked with sodium chloride than with barium chloride, and with barium chloride more than with calcium chloride; while the action is scarcely perceptible with cadmium chloride. The quantity of mercuric chloride formed increases with increasing conc., and with hydrochloric acid, the maximum is attained when the conc. of the acid is 7*N*-HCl. According to H. Hennell, the decomposition of the calomel is complete after boiling it 10 times with a soln. containing an equal weight of sodium chloride. A. Ditte said that it must be admitted that calomel is feebly dissociated by cold water, but much more by hot water; in the presence of an alkali halide a double salt is formed which disturbs the equilibrium of dissociation, and more calomel is dissociated, and this continues until the double salt is also in equilibrium with its components. The potential of the normal calomel electrode is determined by the formation of a little mercuric chloride when a conc. soln. of sodium chloride acts on calomel. According to T. W. Richards and E. H. Archibald, the action of the dissolved mercuric chloride on the decomposition of the calomel is not catalytic; it is conditioned by a state of equilibrium which is a simple function of the square of the conc. of the chloride ions in not too conc. a soln. The general results point to the existence of an ionized complex $HgCl_4''$ in the soln. A. Gockel, and T. W. Richards have measured the temp. coeff. $-d\pi/dT$ of the potential, π, of cells ($-d\pi/dT = \pi/T - Q/\epsilon_0 T$, where Q denotes the change in the total energy—the heat of the reaction—and ϵ_0 is Faraday's constant) with calomel electrodes and soln. of different chlorides: Hg | HgCl, MCl_n, HgCl | Hg. T. W. Richards gives, between 0° and 30°:

	Normal.	$\frac{1}{10}$-normal.	$\frac{1}{100}$-normal.
Hydrochloric acid	0·00033	0·00055	0·00066
Lithium chloride	0·00063	0·00083	0·00100
Sodium chloride	0·00056	0·00078	0·00095
Potassium chloride	0·00061	0·00079	0·00094
Calcium chloride	0·00053	0·00076	—
Strontium chloride	0·00053	0·00074	0·00092
Barium chloride	0·00053	0·00073	0·00092
Magnesium chloride	—	0·00076	0·00096
Zinc chloride	0·00063	0·00078	0·00095
Cadmium chloride	0·00069	0·00082	0·00097
Ammonium chloride	0·00058	0·00085	0·00120

The temp. coeff. increase with dilution, and decrease with rise of temp. Hydrochloric acid and ammonium chloride soln. occupy anomalous positions in the series owing to the presence of hydrogen ions in the former case, and the tendency to form amido-compounds in the latter case. The action of the different chlorides on mercurous chloride is of some importance because of the physiological action of calomel in therapeutics. It follows that in the presence of sodium chloride or hydrochloric acid some calomel will be transformed into corrosive sublimate; the amount of transformation will depend on the conc. of the soln. of alkali chloride rather than on the amount of calomel; and the action will be accelerated by blood corpuscles which act as carriers of oxygen. From this point of view the activity

of calomel is due to its conversion into soluble corrosive sublimate; E. Pollacci assumes that the activity of calomel is due to its being transformed into a very soluble mercuric thiocyanate by the alkali thiocyanates in the system. There is also to be considered the transformation of the calomel in pills and tabloids in the presence of sugar and other organic substances. F. Utz, for instance, says that there is a slow transformation of mercurous to mercuric chloride in tabloids made up with sugar, while R. Vive and T. Budde, and M. Soave say that there is no such change.

L. A. Planché and E. Soubeiran say that when triturated with **iodine water,** calomel forms soluble mercuric iodide and sparingly soluble mercuric iodide. According to F. Gramp, fuming **hydriodic acid** converts calomel into mercuric iodide, which is reduced to mercurous iodide if an excess of hydriodic acid be present. According to O. Wentzky, **alkali bromides** convert calomel quantitatively into mercurous bromide, and, according to K. Klingele, **alkali iodides** act similarly; while in conc. aq. soln. mercury and mercuric iodide separate out. F. Labouré says that aq. soln. of the iodides of magnesium zinc, and iron produce mercurous iodide and a soln. of the metal chloride.

When mercurous chloride is heated with **sulphur,** mercuric sulphide and chloride are formed, and, if the sulphur be in excess, mercuric sulphide and sulphur chloride, S_2Cl_2. According to H. Feigel,[18] a benzene soln. of **sulphur chloride** converts mercurous into mercuric chloride. A. Vogel found that a mixture of **antimony sulphide,** Sb_2S_5, or Sb_2S_3, and mercurous chloride gradually forms mercuric sulphide and antimony trichloride. The action is slow with the powdered materials in air, or under cold water; but under boiling water the action occupies but a few minutes. The same decomposition occurs under ether, turpentine, or oil of lavender, but not under alcohol. P. L. Geiger also studied the reaction, and says that the powders recently precipitated do not react if dried at 100°, but they do so if moist. W. Skey further adds that many other **metal sulphides** decompose calomel—*e.g.* auric sulphide forms gold and mercuric sulphide. A. Vogel stated that cold **sulphurous acid** colours mercurous chloride grey, the boiling acid black. He added that no mercury can be detected in the black precipitate, and he assumed that a **mercury subchloride** is formed, but E. Divers and T. Shimidzu say that no subchloride is formed, and that with purified materials the reaction is so slight that "we doubt whether there is any reaction at all between true mercurous chloride and sulphurous acid." J. A. Smythe and W. Wardlaw found that **sulphur dioxide** oxidizes mercurous to mercuric chloride: $SO_2+4HCl+4HgCl=4HgCl_2+2H_2O+S$; L. M. Stewart and W. Wardlaw found that there is a definite acidity at which the mercurous chloride is not changed, and with less than 0·016*N*-HCl, mercurous chloride is reduced incompletely to mercury. L. P. de St. Gilles says that **alkali sulphites** blacken mercurous chloride converting it into mercury, and a double salt of mercury and the alkali. C. Jones and W. Kirman say that some mercurous sulphite is formed; with a mol of sodium sulphite and one of mercurous chloride, half the mercury separates as metal, and half forms the double salt $Na_2Hg(SO_3)_2$, which is partially precipitated if a conc. soln. of sodium sulphite be employed. A. Vogel stated that **sulphuric acid** neither dissolves nor decomposes mercurous chloride, even after standing together for a long time; but that the hot acid dissolves the salt giving off sulphur dioxide but no hydrogen chloride, and leaves a residue of mercuric chloride and sulphate, the former of which partially sublimes. H. Rose noted that the vapour of **sulphur trioxide** is absorbed by mercurous chloride, forming a transparent mass. G. C. Wittstein found that mercurous chloride dissolves in a soln. of **ammonium sulphate;** while M. Pettenkofer found that a soln. of **potassium sulphate** has no action. A. Vogel noted that when boiled with **calcium sulphate,** mercurous chloride forms mercuric sulphate and calcium chloride, and he adds that **sodium sulphate** behaves in a similar manner. F. Faktor reported that a soln. of **sodium thiosulphate** dissolves mercurous chloride, and the soln. gives a black precipitate when warmed; and J. Schnauss, that mercurous chloride is partially reduced to metallic mercury

by sodium thiosulphate and partly dissolved to form a crystallizable double thiosulphate.

H. Pick [19] says that mercurous chloride is blackened by a soln. of **potassium nitrite,** when the proportion of the former is small and of the latter large—the blackening is due to the separation of mercury and a mercuric salt passes into soln. According to P. F. G. Boullay, and A. Vogel, cold **nitric acid** has no appreciable action on calomel, but the hot acid dissolves that salt, forming nitric oxide and a mixed soln. of mercuric chloride and nitrate: $6HgCl+8HNO_3=3HgCl_2+3Hg(NO_3)_2+2NO+4H_2O$. According to S. Schlesinger, this reaction occurs only with the conc. and warm acid. G. C. Wittstein says mercurous chloride is soluble in a soln. of **ammonium nitrate ;** H. Debray, in hot soln. of **mercurous** and **mercuric nitrates,** and that it crystallizes from the former on cooling ; H. W. F. Wackenroder, and E. Drechsel also noted the solubility of calomel in soln. of mercuric nitrate ; and M. Pettenkofer says that a soln. of **potassium nitrate** has no action.

G. Gore, and E. C. Franklin and C. A. Kraus found that mercurous chloride is soluble in **liquid ammonia ;** and R. J. Kane noted the blackening produced when aqua ammonia acts on the salt, and he believed the product is *dimercurous ammonium chloride*, $Hg_2Cl(NH_2)$, while H. Rose, and F. Isambert believed it to be an addition product, mercurous ammino-chloride, $HgCl.NH_3$. With ordinarily dried materials the action is slow ; it is probable, said J. Sen, that thoroughly dried ammonia and mercurous chloride will have no action on one another, although the black product was shown by C. Barfoed, and H. Saha and K. N. Choudhuri to be a mixture of mercuric chloroamide, $Hg(NH_2)Cl$, with metallic mercury : $2HgCl+2NH_3=Hg+Hg(NH_2)Cl+NH_4Cl$. This opinion that the so-called *black precipitate* is a mixture of metallic mercury with mercuric chloroamide is based on the observation of H. Saha and K. N. Choudhuri that the latter compound can be separated from the mercury in virtue of its solubility in conc. aqua ammonia, and on C. Barfoed's observations that (1) Nearly half the mercury which the precipitate contains disappears as vapour when the precipitate is freely exposed to air, the exposure being under conditions which render chemical decomposition most improbable ; the precipitate at the same time loses its dark colour. (2) Exactly half the mercury exists in the precipitate uncombined, but does not all disappear as vapour, because a little of it acts on the rest of the precipitate, becoming fixed. (3) The white or pale compound left after the mercury has evaporated is the same as that precipitated by ammonia in a soln. of the corresponding mercuric salt—*viz.* $Hg(NH_2)Cl$. (4) The dark precipitates are, therefore, not mercurous ammonium compounds, as heretofore stated, but mixtures of mercuric chloroamide and mercury. J. G. F. Druce supposes the black precipitate to be a compound because when rubbed on copper, it does not amalgamate or perceptibly affect that metal, but later he formulated the reaction $2NH_4OH+Hg_2Cl_2=NH_2HgCl+NH_4Cl+2H_2O+Hg$. The mercurous ammino-chlorides have been studied by J. Sen, C. Barfoed, E. Cohen, etc. According to C. Barfoed, and H. Saha and K. N. Choudhuri, the black product obtained by H. Rose by exposing sublimed mercurous chloride to ammonia gas is not *mercurous ammino-chloride*, $HgCl.NH_3$, as was once supposed, but rather a mixture of free mercury with mercury amido-chloride, $Hg(NH_2)Cl$. F. Isambert measured the dissociation press. of the black product. K. A. Hofmann and E. C. Marburg made **mercurous hydrazine chloride,** $(HgCl)_2N_2H_2$, by shaking a mixture of mercuric chloride with hydrazine sulphate or chloride in aq. soln. M. Adams says that an aq. soln. of *hydroxylamine hydrochloride* dissolves freshly precipitated mercurous chloride without forming a compound, and that a soln. of hydroxylamine in methyl alcohol gradually reduces mercurous chloride.

J. L. Gay Lussac and L. J. Thénard noted that when mercurous chloride is heated with phosphorus mercury is liberated without disengaging chlorine, and H. Davy found that the vapour of *phosphorus* converts mercurous chloride into mercury phosphide, and phosphorous chloride. According to A. Baudrimont, *phosphorus pentachloride* converts mercurous chloride into the mercuric salt, which then unites

with the excess of phosphorus pentachloride, forming a compound $3HgCl_2.2PCl_5$; phosphorus trichloride is liberated during the reaction. When heated with one-third its weight of *arsenic*, F. Capitaine obtained a sublimate with yellow tetrahedral crystals of arsenic mercuri-chloride, AsHgCl, a compound which is decomposed by hot water, forming an amalgam with arsenic, arsenious oxide, and hydrogen chloride; it is also decomposed by heat into mercury, arsenic, and arsenic trichloride. According to Z. Klemensiewicz, mercurous chloride does not dissolve in molten *antimony trichloride*.

J. L. Gay Lussac and L. J. Thénard [20] reduced mercurous chloride to the metal by heating it with carbon, and W. A. Lampadius also decomposed the vapour of calomel by red-hot carbon. According to F. von Kügelgen, mercurous chloride reacts with about one-seventh its weight of *calcium carbide* when warmed to start the reaction; the whole mass then glows red hot, but the reaction is so slow that most of the mercury remains with the slag. C. W. Scheele found that an aq. soln. of *hydrocyanic acid* blackens mercurous chloride furnishing metallic mercury, mercuric cyanide, and hydrochloric acid, a reaction which L. Mailhe, and E. Riegel represented by the equation: $2HgCl+2HCy=Hg+HgCy_2+2HCl$. E. Regimbeau says the black colour is a mixture with mercury as a kind of emulsion. The reaction is much more complex than this equation assumes. J. A. Buchner says a part of the mercurous chloride remains undecomposed, and L. Fouquet, that the acid which is produced brings the reaction to a standstill if it is not neutralized, for while hydrochloric acid is displaced by hydrocyanic acid in dil. soln., the reverse action occurs with conc. soln. D. Vitali says no mercuric chloride is formed; M. H. Deschamps says some ammonia or ammonium cyanide is produced; L. Mailhe says formic acid is produced; E. Soubeiran, and M. H. Deschamps say an organic compound is also formed; A. A. B. Bussy and H. Buignet, and E. Esteve say that some mercurous chloride is converted into mercury and mercuric chloride, and the latter passes into soln., but if sufficient hydrocyanic acid is used, the reaction is quantitative. E. Wollschläger believes the first action with dil. hydrocyanic acid can be represented: $2HgCl+HCy=Hg+HgCyCl+HCl$. M. Beranger, however, thinks the presence of mercuric chloride is doubtful. M. Cheynet emphasized that the association of preparations of hydrocyanic acid with calomel in medicines may give rise to chemical reactions in which mercuric cyanide is formed, but this is not more toxic than the hydrocyanic acid which it replaces; and G. Patein has shown that the toxicity of a dil. soln. of hydrocyanic acid—1·4 grms. per litre—is virtually the same as it is in contact with a great excess of calomel when the acid formed in the latter case has been neutralized. According to A. Ditte, calomel is decomposed by a conc. soln. of *potassium cyanide*, forming a potassium mercuric cyanide, potassium chloride, and mercury by an exothermal reaction. E. Pollacci said that *hydrothiocyanic acid*, HSCy, is present in the saliva, and reacts with calomel and forms mercuric thiocyanate.

Mercurous chloride gives up its chlorine to many of the base metals both in the dry and humid states. J. L. Gay Lussac and L. J. Thénard [21] reduced calomel to the metal by heating it with *potassium* or *sodium*. When boiled with *copper* and water, A. Vogel noted that the soln. becomes green and the copper is covered with a black film from which hydrochloric acid extracts copper oxide leaving a residue of mercury, and H. Bonnewyn noted that a clean strip of copper is not changed in contact with calomel wetted with alcohol or ether, but if as little as $\frac{1}{50000}$th of mercuric chloride be present the copper is blackened. According to K. Seubert and A. Schmidt, when calomel is heated with *magnesium* filings, mercury and some magnesium amalgam are formed; when the two suspended in water are boiled together the calomel is reduced to mercury; but in contact with magnesium and hydrochloric acid, calomel is but slowly attacked, and after a long time some mercury oxide is formed. H. Rose also says that calomel is reduced to mercury when boiled with many metals, but not with *zinc*. The heat of formation of mercurous chloride is greater than that of silver chloride, and the reduction of mercurous chloride by

silver is therefore an exothermal process, and J. N. Brönsted measured the potential π, and the temp. coeff. $d\pi/dT$ of the cell Ag | AgCl, $KCl_{aq.}$, HgCl | Hg, and hence calculated U, the heat effect of the reaction $Ag+HgCl=Hg+AgCl$ from Helmholtz's equation : $T(d\pi/dT)=\pi-U$, and found it to rise from 1300 cals. at 23° to 1550 cals. at 80°. F. Pollitzer's value is too low. A. Colson showed that the reaction between silver and mercurous chloride in a sealed vacuous tube between 150° and 300° is a reversible reaction limited by the press. of mercury vap.

According to R. J. Kane,[22] when calomel is heated with dry *alkali hydroxides*, or the oxides or hydroxides of the alkaline earths, mercury, oxygen, and the alkali chloride are formed : $4HgCl+4KOH=4KCl+2H_2O+O_2+4Hg$; and with aq. soln. of the alkali hydroxides black mercurous oxide is formed : $2HgCl+2KOH=Hg_2O+H_2O+2KCl$. J. A. Buchner noted that the filtrate still retains some mercurous salt, and I. Bhaduri added that the decomposition is incomplete, but progresses nearer completion by raising the temp. ; and it can be completed by raising the temp. to the b.p., and repeating the operation with fresh alkali. C. Barfoed argued that the precipitate is a mixture of mercury with mercuric and mercurous oxides in varying proportions, and not of mercuric oxide and mercury ; sometimes as much as 81 per cent. of mercurous oxide is present. The mercurous oxide is oxidized by air at ordinary temp. in light and in darkness. The precipitate gradually becomes paler owing to the volatilization (not oxidation) of the finely divided mercury. W. Herz measured values of $K=[KOH]^2/[KCl]^2$ and of $K_1=[KOH]/[KCl]$ in the balanced reaction : $2HgCl+2KOH\rightleftharpoons Hg_2O+2KCl+H_2O$, and found at 25° for K_1, numbers ranging from 0·0152 to 0·0166.

According to A. von Dieterich and L. Wöhler, if 0·001*N*-KOH to which phenolphthalein has been added, be shaken with mercurous chloride, the red colour disappears on account of neutralization, and the mixture becomes grey on account of the formation of mercurous hydroxide ($HgCl+OH'=HgOH+Cl'$). With 0·01*N*-KOH mercurous chloride becomes grey, but the red colour produced by phenolphthalein is not destroyed because the chlorine ions reach such a conc. that the above reaction is reversed. The addition of potassium chloride produces the same effect on the 0·001*N*-KOH. If a few drops of a sat. soln. of potassium chloride be added to the dilute potassium hydroxide soln. which has been shaken with mercurous chloride, the red colour is reproduced. A mixture of equal volumes of 0·01*N*-KOH and sat. potassium chloride soln. has no action on mercurous chloride, which remains perfectly white. If any of these soln., to which mercurous chloride has been added without causing the disappearance of the red colour of the phenolphthalein, be warmed, the red colour disappears and reappears on cooling.

H. Hager says that soln. of sodium hydrogen carbonate, $NaHCO_3$, do not alter calomel, but if a trace of normal sodium carbonate, Na_2CO_3, be present, the calomel becomes grey. The reaction with soln. of *sodium carbonate* is symbolized : $2HgCl+Na_2CO_3=Hg_2CO_3+2NaCl$, and, according to G. Patein, the presence of sodium chloride accelerates the decomposition. W. Herz found at 25° for $K=[Na_2CO_3]/[NaCl]^2$, numbers ranging from 1·30 to 1·65. G. Vulpius has studied the transformation of mercurous into mercuric chloride when mixed with sugar and sodium hydrogen carbonate. G. C. Wittstein reported that soln. of *ammonium carbonate* colour mercurous chloride grey and quickly dissolve it, leaving a small residue of metallic mercury. According to J. A. Buchner, *magnesium carbonate* has no action on calomel in the presence of cold water, but when boiled, carbon dioxide is evolved, mercury separates out, and a soln. of magnesium mercuric chloride is formed ; while, according to A. Vogel, when calomel is heated with water and magnesium or *calcium carbonate* the action is similar, and mercurous (or mercuric) oxide, calcium chloride, mercury, and carbon dioxide are formed ; *barium and strontium carbonates* act similarly, but the action is more feeble.

A. Vogel found that a soln. of *stannous chloride* reduced calomel to the metal, slowly at ordinary temp., and rapidly when heated. F. Capitaine prepared dendritic crystals, **stannous tetrachloromercurite,** $SnCl_2.2HgCl$, by heating 75 per cent. tin amalgam with mercurous chloride.

The mixture of the tin amalgam with six times its weight of mercurous chloride is

heated to about 250° in a large glass retort. When the frothing ceases, the retort is cooled and then broken. The grey spongy mass is separated from the mercury and pulverized. The powder is heated in a stoppered flask to a temp. not exceeding the b.p. of mercury. When the fumes of stannous chloride have ceased to come off, the desired salt sublimes, and stannic chloride and mercury remain behind. The flask is broken to cool the sublimate.

When the salt is heated part decomposes and part sublimes; when treated with water there is some decomposition and mercury separates. The *butyrum stanni* of the alchemists contained variable proportions of stannous and mercurous chlorides. W. von Gulewitsch prepared **aluminium benzene chloromercurite,** $AlCl_3.HgCl.C_6H_6$, from a benzene soln. of the component salts. J. Schnauss [23] said that a mixed precipitate of silver and mercurous chlorides is not sensitive to light, and likewise the precipitate obtained by adding a soln. of mercurous chloride to one of silver nitrate, for it, too, always contains a little mercurous chloride. H. C. Jones obtained a white powder, which has been regarded as AgCl.3HgCl, by the action of silver amalgam on mercurous chloride. The yellow or red earthy mineral *bordosite* from Chili is regarded as a compound AgCl.2HgCl. H. C. Jones made a product considered to be **silver dichloromercurite,** HgCl.AgCl, by triturating precipitated silver with a large excess of mercuric chloride, and after 3 or 4 weeks, heating the mixture in a long-necked flask for 12–20 hrs. on a water-bath. The product is separated from silver and mercurous chloride by levigation with water. The white product has a sp. gr. 6·495; it is blackened by ammonia. According to H. C. Jones, it is probable that $NHAgHg_2Cl$ and $NH_2AgHgCl$ are formed. According to N. Antoni and G. Turi, the blackening is due to the formation of metallic silver. Conc. hydrochloric acid extracts half the mercury.

C. Meineke said that mercurous chloride is oxidized to the mercuric salt by *ferric salts,* and also, but more slowly, by *potassium permanganate.* O. Aschan and G. Borenius [24] state that 95 per cent. *formic acid* dissolves 0·02 per cent. of mercurous chloride which has been dried at 100°—so that 100 c.c. of the soln. contain 0·018 grm. of HgCl—water alone dissolves but 0·0003 per cent. of HgCl, and calomel is reduced to the metal by a boiling soln. of *potassium formate.* According to G. Patein, *alkali acetates* act like the chlorides. J. Schoras found calomel to be incompletely reduced when heated with *oxalic acid,* but in sunlight, the reaction progresses to an end. H. Zilgien noted that when 3 drops of *lactic acid* and 25 c.c. of aqua ammonia are added to 0·05 grm. of calomel suspended in 10 c.c. of water, 0·008 grm. is converted into mercuric chloride—neither ammonia, lactic acid, nor ammonium lactate act in this way.

Calomel was formerly said to be insoluble in *alcohol* and *ether;* according to R. Vive and T. Budde,[25] calomel is partially decomposed by 90 per cent. alcohol; J. L. Lassaigne detected no mercuric chloride in the ether extract of calomel; and H. Maclagan says that alcohol, ether, and chloroform dissolve very small amounts of mercurous chloride which is at the same time decomposed. L. I. Shaw has measured the conductivity of soln. of calomel, in methyl alcohol, acetic anhydride, acetone, ethyl acetate, acetyl chloride, epichlorhydrin, dimethyl sulphate, benzonitrile, aniline, and salicylaldehyde.

F. B. Hofmann found that when calomel is shaken with water, and benzene, toluene, or chloroform, the powder is retained at the surface of contact of the two liquids owing to the partial wetting of the powder by both liquids. H. von Euler and G. Zimmerlund studied the adsorption of mercurous ions by mercury from soln. of mercurous chloride.

Calomel is insoluble in *acetone* and *benzonitrile* (A. Naumann, and L. I. Shaw said soluble); *ethyl acetate* (M. Hamers, and L. I. Shaw said soluble); *petrol ether, decane, hexane,* or *carbon disulphide* (W. von Gulewitsch); calomel is sparingly soluble in *nitromethane* at ordinary temp. (J. Kozak and G. Mariasz); in a soln. of *ammonium succinate* (G. C. Wittstein); in *chloroform, bromoform, ethyl bromide,* and *ethylene bromide* (O. Sulc); calomel is soluble in *benzene* and other *aromatic hydrocarbons, amylene, caprylene,* and *turpentine* (W. von Gulewitsch); *pyridine* (A. Werner). According to S. J. Bendiner, a mixture of calomel and *iodoform* decomposes at ordinary temp. in light even when the

actinic rays are cut out, and when the mixture has stood for some time, according to O. Schweissinger, it is completely converted into a mixture of chloroform and mercuric iodide. H. Ost and A. Mente noted the formation of a crystalline compound with *oxamide*. According to E. Baroni and O. Borlinetto, calomel forms coloured compounds with the salts of *quinine*, but not with the alkaloid itself; it also reacts similarly with *pilocarpine*, *cocaine*, and *heröine*. E. Pollacci says it is not reduced by *formaldehyde*, *uric acid*, *hippuric acid*, *and glycose*. H. D. Gibbs found calomel is blackened by liquid *methylamine*, and crystals are formed when the soln. is cooled with liquid ammonia.

Calomel is the *hydrargyri subchloridum* of the pharmacopœia; it is employed in making salves—with lard it forms the *ungentum hydrargyri subchloridi* of the pharmacopœia. If pure it is not toxic, but in presence of chlorides many regard it as a poison. Mixed with antimony sulphide guaiacum resin, and castor oil, it is the *pilula hydrargyri subchloridi composita* or Plummer's pill of the pharmacopœia used as a purgative.

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§ 12. Mercuric Chloride

The history of mercuric chloride, $HgCl_2$, or corrosive sublimate, has been discussed in the preceding section. L. Besnou [1] reported its occurrence in the Atacama desert (Iquique), and A. Frenzel in the volcanic district of one of the Molucca Islands; but there is room for doubt since the reports are based on a few qualitative trials.

The preparation of mercuric chloride.—(1) *By chlorinating mercury.*—As indicated in connection with mercurous chloride, mercuric chloride is formed by heating mercury in an excess of chlorine gas. C. Göpner [2] made it by shaking mercury with chlorine hydrate; and C. L. Berthollet, by passing a current of chlorine into a vessel containing mercury and water. A. Lottermoser prepared what he regarded as *colloidal mercuric chloride* by the action of chlorine water on a colloidal soln. of mercury until the liquid became colourless. E. Trutzer introduced chlorine under a small press. into a closed vessel containing mercury with or without water or other liquid medium, and kept continuously agitated so as to prevent the formation of a protective skin on the unattacked mercury. The temp. (say 20°) is kept below the volatilization point of mercury. The Saccharinfabrik patented a process for preparing mercuric chloride in which chlorine is passed through a quartz tube into boiling mercury contained in a quartz vessel. The mercuric chloride vapour is carried by a current of cold air into a condensing tower, where it collects in a voluminous mass of acicular crystals free from calomel. E. G. Moeys heated mercury, hydrogen chloride, and a silicate to the sublimation temp. The silicate acts as a stimulant and may be used over again. Mercuric chloride is also formed when mercury is dissolved in hot hydrochloric acid containing a little nitric acid, and the mixture warmed until the precipitated calomel is redissolved; the crystals obtained on evaporating the soln. are recrystallized from hot water. L. Mailhe detected the formation of mercuric chloride when an aq. soln. of ammonium, potassium, or sodium chloride is allowed to act on mercury in the presence of air. A. J. von Oettingen denied this reaction, but it was confirmed by K. Voit. The reaction was regarded as of great importance as offering a possible explanation

of the physiological action of mercury, and the insoluble mercurous compounds on animals and man.

The process described by the Latin-Geber in the thirteenth century was in use for a long time. Geber said :

> Thoroughly mix a pound of mercury, two pounds of vitriol, a pound of calcined rock alum, a pound and a half of common salt, and a fourth part of saltpetre, and then sublime. Collect the white and dense product which collects on the upper parts of the vessel. . . . If the product of the first sublimation be turbid or unclean—which may be the result of your own negligence—it must be resublimed.

According to G. F. Hildebrandt, in the old Dutch process, three parts of mercury, two of sodium chloride, two of nitre, and four of calcined ferrous sulphate were triturated together, and then sublimed: $Hg+2NaCl+2KNO_3+Fe_2O(SO_4)_2=Na_2SO_4+K_2SO_4+Fe_2O_3+HgCl_2+2NO_2$; the nitrous fumes were condensed in receivers containing water, and sold as *sublimate water* for the preparation of mercuric oxide—the nitre, added G. F. Hildebrandt, served no useful purpose. A. F. de Fourcroy (1792), and P. L. Geiger recommended similarly treating a mixture of 10 parts of mercury, 8 of sodium chloride, 6 of manganese dioxide, 11 of sulphuric acid, and 3 of water: $Hg+2NaCl+MnO_2+2H_2SO_4=HgCl_2+Na_2SO_4+MnSO_4+2H_2O$—the yield, added P. L. Geiger, is 12·24 parts of corrosive sublimate. T. Fairley converted calomel into mercuric chloride by boiling it with an acidified soln. of an alkali hypochlorite. C. Schantz passed mercury through an atm. of chlorine into a bath of a liquid which does not readily absorb chlorine.

(2) *By chlorinating mercuric oxide.*—E. Pelouze projected mercuric oxide into a flask of chlorine; the formation of mercuric chloride was accompanied by the disengagement of heat and light. It is also formed when mercuric oxide is dissolved in hydrochloric acid; J. J. Berzelius, L. Mailhe, and J. Fonberg, obtained it by heating mercuric oxide with a soluble chloride, *e.g.*, mercuric chloride is formed when either mercurous or mercuric oxide is kept in contact with a soln. of sodium chloride between 40° and 50° for say 24 hrs. The liquid becomes alkaline owing to the formation of sodium hydroxide: $HgO+2NaCl+H_2O=2NaOH+HgCl_2$. J. J. Berzelius used a soln. of magnesium chloride and found some magnesium hydroxide was precipitated; R. Wagner recommended the mother liquors (magnesium chloride) from carnallite; C. Hochstetter used a soln. of calcium chloride, and calcium hydroxide was precipitated. L. H. F. Melsens, and J. Fonberg noted that if the chlorides of the alkaline earths are used, the excess can be removed by passing a current of carbon dioxide. H. Rose noted that mercuric oxide slowly precipitates manganese quantitatively as manganese oxide from soln. of manganous chloride; lead oxide from lead chloride; zinc oxychloride from zinc chloride; cupric oxide from cupric chloride; nickel oxide from nickel chloride; cobalt oxide from cobalt chloride; and a ferric oxychloride from ferric chloride. J. R. Spielmann, and P. F. Delkeskamp sublimed a mixture of mercuric oxide with ferrous sulphate and sodium chloride.

(3) *By the double decomposition between chlorine or the chloride or other mercuric salt.*—Mercuric chloride is formed during the double decomposition of mercuric salts by a metal chloride—*e.g.* A. G. Monnet made it by the action of an aq. soln. of sodium chloride on mercuric nitrate. The reaction between soln. of mercuric sulphate and sodium chloride is exothermal. E. Rupp and W. Klee add that the product obtained by treating mercuric sulphate with barium or calcium chloride is not satisfactory since basic salts are formed which contaminate the product. L. Mailhe also made mercuric chloride by the action of soln. of the metal chlorides on various mercurous salts—*e.g.* by a soln. of sodium chloride on mercurous chloride, bromide, iodide, nitrate, or tartrate. A boiling conc. soln. of mercurous nitrate is mixed with conc. hydrochloric acid so long as precipitation occurs; and the precipitate is boiled with as much hydrochloric acid as was used in its formation: $HgNO_3+2HCl=HgCl_2+H_2O+NO_2$. The crystals of mercuric chloride separate on cooling, and they can be recrystallized from hot water.

J. von L. Kunckel, and G. F. Boulduc heated equal parts of mercurous sulphate and sodium chloride. This process is employed on a manufacturing scale. A little manganese dioxide—about one-tenth of the weight of mercurous sulphate employed—is preferably added to J. von L. Kunckel's mixture to prevent the formation of calomel from the mercurous sulphate which may be present. The manganese dioxide reacts with the sodium chloride, giving off chlorine which converts mercurous to mercuric chloride. H. Fleck says that if the sublimation be conducted in an atm. of hydrogen chloride, the product will be free from mercurous chloride.

The mixture is sublimed on a large scale in long-necked glass balloons which are placed on iron plates, surrounded up to their necks with sand and gently heated to drive off all the moisture. While the contents of the glass subliming pots are being dried, hoods leading into a flue are placed over the necks. The hoods are then replaced by small inverted conical condensers and sufficient sand is removed to uncover the upper half of the body of the flask. The heat is increased until the whole of the mercuric chloride has sublimed, and finally raised sufficient to make the crust of sublimate coherent, but not to melt it. When cold the glass balloons are broken and the cake of sublimate removed. A little less volatile calomel may collect on the lower part of the cake; this is removed and added to a subsequent sublimation. The operation is conducted in a good draught because of the very poisonous character of the fumes.

E. F. Anthon proposed to sublime a mixture of calomel with an excess of potassium bisulphate and sodium chloride. H. Boerhaave sublimed a mixture of mercuric nitrate, sodium chloride, and roasted ferrous sulphate.

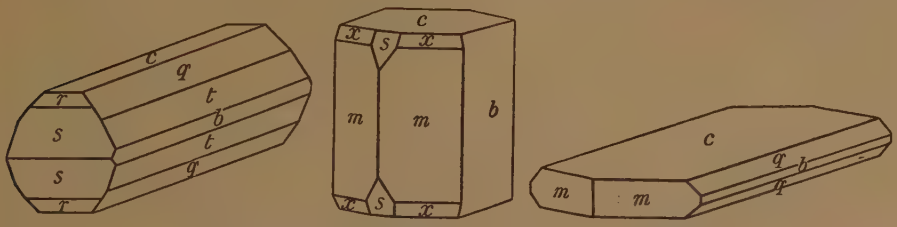
W. Sievers saturated a soln. of mercuric nitrate of sp. gr. 1·197 with chlorine gas, and recrystallized the precipitated mercuric chloride many times from hot water. E. Chauvenet found that carbonyl chloride, $COCl_2$, at 350°, converts mercuric sulphide, very rapidly into mercuric chloride. R. Wagner treated mercuric sulphate with hydrochloric acid, and after crystallizing out the mercuric chloride, he used the mother liquid to redissolve more mercury; or he treated mercuric sulphate with barium hydroxide, and extracted the mercuric oxide with hydrochloric acid.

Mercuric chloride can be tested for impurities in the following manner: A soln. of 5 grms. of mercuric chloride in 100 c.c. of water and 5 c.c. of hydrochloric acid of sp. gr. 1·124 is treated with hydrogen sulphide until all the mercury is precipitated; the clear filtrate, when evaporated to dryness on the water-bath, should not give a weighable residue. The precipitate can be agitated with 5 c.c. aqua ammonia, and 45 c.c. of water and filtered; if arsenic be absent, the filtrate will not give a yellow coloration when acidified with hydrochloric acid. If calomel be absent, a gram of the sample should dissolve completely in 25 c.c. of ether. O. Wolff noted that the orange fluorescence of some specimens of mercuric chloride is due to the contained mercurous chloride, and that the latter compound is always formed during the sublimation of mercuric chloride.

W. L. Hardin purified mercuric chloride by dissolving it in hot water, filtering, evaporating to crystallization, drying the crystals, and then subliming them from a porcelain vessel into a glass tube; and repeating the whole process once again. Some prefer to conduct the sublimation in a stream of dry chlorine so as to ensure the conversion of mercurous to mercuric chloride. K. Charitschkoff made **colloidal mercuric chloride** by the action of hydrogen chloride on a soln. of mercuric naphthenate in a hydrocarbon containing an excess of naphthenic acid.

The properties of mercuric chloride.—Commercial sublimate usually has the form of a translucent crystalline crust. W. J. Luczizky [3] says that the sublimed **crystals** are bipyramids belonging to the rhombic system, and have axial ratios $a : b : c = 0{\cdot}7251 : 1 : 1{\cdot}0697$. E. Mitscherlich and H. J. Brooke also measured the crystal constants (Fig. 11); E. Mitscherlich and W. J. Luczizky obtained crystals with the habit illustrated in Fig. 12, by slowly cooling hot alcoholic or aq. soln. with a little zinc chloride in soln. The latter addition was also recommended by J. W. Retgers. H. Arctowsky obtained plate-like crystals by heating aq. soln. in a sealed tube to 130°–200°; and W. J. Luczizky obtained crystals with the habit

illustrated in Fig. 13, from soln. of mercuric chloride and bromide. According to W. J. Luczizky, and J. S. van Nest, it exists in two different rhombic forms of different stability, the normal stable form, and with mixtures of mercuric bromide. R. Marc



FIGS. 11 to 13.—Habits of Mercuric Chloride Crystals.

has studied the speed of crystallization from aq. soln.; and E. F. Farnau the crystalloluminescence of the mercury halides.

The reported values of the **specific gravity** vary from J. H. Hassenfratz's [4] 5·1398 to L. Playfair and J. P. Joule's 6·223. J. S. van Nest's value 5·45 ± 0·025 (20°) is fairly representative. N. Orloff gave the **molecular volume**, 50·97. C. Tourneux gave 5·43 for the sp. gr. at 15°/15°, 0·184 for the sp. vol., and 50 for the mol. vol. H. W. Foote and N. A. Martin gave 4·36 for the sp. gr. of the molten salt at 282°; and, according to E. B. R. Prideaux, the sp. gr. of the liquid falls from 4·398 at 281° to 4·238 at 357°, and for $\theta°$ between 280° and 335°, the sp. gr. $D=4·400-0·002218(\theta-280)$. 100 vols. of the elements at 860 mm. become 101·9 on combustion; at 760 mm., 101·8; and at 560 mm., 101·7; and the sp. gr. 4·380 of mercuric chloride at 560 mm. press. becomes 4·348 at 760 mm., and 4·336 at 860 mm. W. Biltz gave 49·8 for the mol. vol. A. Reis and L. Zimmermann gave 2·0 for the **hardness.**

The **melting point** given by J. S. van Nest [5] is 265°; by R. Kempf, 283°; 273° by J. C. G. de Marignac; by W. P. A. Jonker, and by T. Carnelley and W. C. Williams, 277°. The latter says that if the superincumbent press. is below a certain minimum value, called the critical press., it is impossible to melt mercuric chloride, ice, etc. The **boiling point** is 302·5°, according to F. M. G. Johnson; 302·5°, according to T. Carnelley; 296°, according to J. C. G. de Marignac; and 307°, according to F. Freyer and V. Meyer. The m.p. and b.p. are thus fairly close together, and at its m.p. mercuric chloride rapidly volatilizes. M. Faraday, H. Arctowsky and C. Zenghelis said that this salt volatilizes perceptibly at ordinary temp., while E. Riegel said that neither the solid salt nor the aq. soln. loses mercuric chloride by volatilization at ordinary temp. L. Vignon reported a loss of 4 per cent. during 60 hrs'. heating at 80°; O. Sulc, 6·3 per cent. during 6 hrs'. at 101·5°; and H. Arctowsky found layers 2 mm. deep in similar dishes 2 cms. diameter lost in 20 hrs. 0·0011 grm. at 56·5°; 0·0089 grm. at 79°; and 0·28 grm. at 125°. R. Kempf noted the volatilization is much more rapid under reduced press. W. A. Hargreaves and W. T. Rowe took advantage of the low volatilizing temp. of mercuric chloride to estimate the amount employed with some explosives—gelignite, blasting gelatine, etc. The explosive is ground up with an equal weight of French chalk, and heated in a glass flask in a water oven while a current of air is aspirated through the flask and then into an absorption apparatus containing dil. sulphuric acid, which collects the mercuric chloride. O. Sulc noticed that when an aq. soln. of mercuric chloride is evaporated some of the salt is volatilized with the steam, and this the more, according to A. Minozzi, the more conc. the soln.; but E. Esteve said that the conc. has little or no influence while the form of the vessel has a marked influence. M. Lehmann, F. Utz, and J. Volhard noted that the presence of sodium chloride prevents the volatilization of mercuric chloride from alcoholic soln. G. H. Bailey also noted that the volatilization of mercury chloride

occurs during the evaporation of ethereal as well as of aq. soln. L. Rotinjanz and W. Suchodsky compute the **critical temperature** to be 703°, and H. Rassow found 703°. The value calculated from T. E. Thorpe and A. W. Rucker's formula $(T_bV_b-273)/2(V_b-1)$, where T_b denotes the absolute b.p., 577·4° K.; and V_b the sp. vol. at the b.p. C. M. Guldberg found the ratio T_b/T_c, where T_c denotes the absolute critical temp. is approximately equal to 0·67 for a number of corresponding liquids; for mercuric chloride, $T_b/T_c=0·59$. M. Prud'homme, and E. van Aubel studied the relation between the critical temp., the b.p., and the m.p.

The **vapour pressure** has been measured by V. von Richter (200°–279°), E. B. R. Prideaux (from 286·1° to 309·0°), and F. M. G. Johnson. The last-named gave for the vap. press. p in mm. of mercury at

	152°	195°	231°	256°	262°	275°	278°	283°	302°
p	3	20	82	198	237	375	421	481	754

When plotted, there is a distinct break in the slope of the vap. press. curve at the m.p., 277°. E. Wiedemann, K. Stelzner, and G. Niederschulte found the vap. press. at 60° to be 0·003 mm.; at 100°, 0·10 mm.; at 140°, 1·35 mm.; and numbers rather lower than those of F. M. G. Johnson for temp. up to 300°. From R. Clausius' formula $d \log p/dT=Q/RT^2$, assuming that the vapour is not dissociated, F. M. G. Johnson calculated the **latent heat of vaporization** between 760 mm. and 800 mm. to be 14·63 Cals.; E. B. R. Prideaux, 13·91 Cals.; the former gave for **Trouton's constant** 25·44, the latter 24·1. For a liquid boiling between 304° and 354°, the normal value is 22·19; and it is therefore inferred that the liquid is associated to some extent but not so greatly as with water and the alcohols for which $Q/T=26$. W. Ramsay's constant, T_1/T_2, is 1·040 (750 to 450 mm.). According to E. Beckmann, the **latent heat of fusion** is 16·9 cals. per gram.

The **vapour density,** according to E. Mitscherlich, is 9·8; and R. Rieth's values correspond with the **molecular weight,** 278·2; the calculated value for $HgCl_2$ is 271. A. Scott obtained a vap. density corresponding with a mol. wt. 155·6 at high temp. The mol. wt. calculated from the lowering of the f.p. of aq. soln., by E. Beckmann, and W. Biltz, is 266, and in alcoholic soln., 264. The mol. wt. calculated from the raising of the b.p. of aq. soln. by W. Landsberger, is 263, and of alcoholic soln. by W. Landsberger and A. W. C. Menzies, 269; of dil. ethereal soln. by R. Lespieau, approximates to that required for the undissociated mol., but in conc. soln. the value is greater; in acetone soln., P. Dutoit and L. Friderich found 271; and H. C. Jones, 269·5, and the value was not appreciably affected by dilution. In methyl acetate soln., H. Steiner found 248; in ethyl acetate soln., M. Hamers and A. Naumann found 262; in methyl sulphide soln., A. Werner, 251; in ethyl sulphide soln., A. Werner, 279; and in benzonitrile soln., A. Werner, 269; in urethane soln., N. Castoro, 271; in ethylurethane soln., L. Mascarelli and M. Ascoli, 256; in pyridine soln., J. Schröder, 287; and, added P. Walden and M. Centnerszwer, the mol. wt. in dil. soln. of pyridine is normal, in conc. soln. it is less than normal, and this the more the greater the conc. The b.p. of soln. of mercuric chloride in many organic solvents are in agreement with a non-associated mol. $HgCl_2$, but in aq. soln. the data are so discordant among themselves that the conclusions are indefinite. The distribution ratio of mercuric chloride between benzene or toluene and water agrees with an associated mol. Hg_2Cl_4 or $Hg.HgCl_4$ in aq. soln., a conclusion in agreement with observations on the f.p. of aq. soln.

H. V. Regnault's value for the **specific heat** of the solid from 13° to 98° is 0·0689; and J. N. Brönsted's value from 0° to 19° is 0·05019; the latter also gave 11·83 for the mol. ht. K. Jauch found the sp. ht. of soln. containing 0·5, 1·0, and 2·0 eq. of mercuric chloride per litre to be respectively 0·9834, 0·9675, and 0·9543 at 18°. According to A. Blümcke, the sp. ht. of aq. soln. containing 1·02, 2·07, and 3·03 per cent. of $HgCl_2$ are respectively 1·003, 0·983, and 0·961; and for 3·12, 9·87, and 17·26 per cent. alcoholic soln., respectively 0·667, 0·632, and 0·595. W. Timofejeff found the sp. ht. of soln. containing 25, 50, and 100 mols of methyl alcohol

per mol of $HgCl_2$ to be 0·50776, 0·55406, and 0·58236 respectively, and with ethyl alcohol, 0·52403, 0·55683, and 0·57865 respectively between 10° and 50°.

The **heat of formation,** according to J. Thomsen,[6] is (Hg, Cl_2)=63·16 Cals.; W. Nernst gave 53·3 Cals.; and R. Varet gave 53·3 Cals. and later 49·8 Cals. J. Thomsen found for the **heat of solution** ($HgCl_2$, Aq., —3·3 Cals., M. Berthelot, —3 Cals.; J. Thomsen also gave for the **heat of neutralization** $HgO+2HCl_{aq.}$ =18·92 Cals.; $HgO+2HCl_{gas}$=56·86 Cals.; $2HgCl+Cl_2$=43·77 Cals.; and $Hg(NO_3)_{2aq.}+2KCl_{aq.}$=12·93 Cals. M. de K. Thompson gave —42·600 cals. for the **free energy** of formation of mercuric chloride; and M. S. Sherrill gave 19·13 Cals. for energy of formation from its ions.

The **index of refraction** of aq. soln. of mercuric chloride has been measured by C. Cheneveau,[7] and by M. le Blanc and P. Rohland. The two latter found for 6·04 and 6·03 per cent. aq. soln. the respective indices of refraction 1·3382 and 1·3383; the respective **molecular refractions** by Gladstone and Dale's formula 19·25 and 19·42; and by Lorenz and Lorentz's formula 11·26 and 11·36. For 6·52 and 5·44 per cent. soln. in alcohol, the indices of refraction are 1·3666 and 1·3657; with the eq. refractions by Gladstone and Dale's formula 19·58, and 19·56, and by Lorenz and Lorentz's formula 11·24 and 11·23. Similarly, for 21·05 and 10·94 per cent. soln. in acetone, the respective indices of refraction 1·3793 and 1·3693; and Gladstone and Dale's formula 20·15 and 20·29, and by Lorenz and Lorentz's formula 11·55 and 11·65. O. Schönrock's values for the specific **electromagnetic rotatory power** for the plane of polarization, are:

	Water.	Alcohol.	Pyridine.	Amyl alcohol.	Acetone.
Per cent. $HgCl_2$ . .	4·5256	23·5489	17·5312	10·9948	36·3488
Sp. gr. . . .	1·03806	0·99885	1·15228	0·89550	1·15854
Rotatory power . .	0·8599	0·8374	0·9665	0·8922	0·8290

B. O. Pierce studied the **emission spectra** of the three mercuric halides—chloride, bromide, and iodide, and found that the emission spectra of mercurous and mercuric chlorides have bands lying between the yellow and green mercury lines with a mid-point at about 5800. The continuous spectrum in the green region has many fine weak lines. He inferred that the emission spectra of the two heated mercury chlorides are the same, owing to the fact that mercurous chloride dissociates into mercuric chloride and chlorine, and that the continuous spectrum of each compound is due to mercuric chloride. A. C. Jones extended these results into the ultra-violet. E. J. Evans studied the **absorption spectrum** of mercuric chloride vapour. According to J. A. Wilkinson, mercuric chloride has a greenish **fluorescence,** and it shows a luminosity in ultra-violet light only if contaminated with mercurous chloride. A. L. Hughes has measured the **photoelectric effect** of mercuric chloride, and G. P. Dima found it to be smaller than for the corresponding bromide or iodide. According to W. Matthies,[8] the **glow discharge** between platinum electrodes does not decompose the vapour of mercuric chloride, provided the current is not great enough to give the spectrum lines of mercury. Copper, iron, aluminium, and mercury electrodes cause decomposition without an electric current; a tantalum electrode is disintegrated. The glow discharge resembles that with the elementary gases generally; the potential gradient is higher than for nitrogen as are also the cathode and anode falls. According to P. D. Foote and F. L. Mohler, the **ionization potential** of mercuric chloride vapour is 12·1 volts.

S. Meyer found the **magnetic susceptibility** to be $0·17\times10^{-6}$ unit of volume or —0·15 unit of mass. C. Fritsch measured the **electrical conductivity** of pressed plates of solid mercuric chloride. M. Faraday noted that while mercuric chloride did not conduct the voltaic current in the solid state, it did conduct when fluid, but, according to J. W. Clark and W. Hampe, the electrical conductivity of molten mercuric chloride is small, and a current can decompose the salt into mercurous chloride and chlorine. H. W. Foote and N. A. Martin found the sp. conductivity of the molten salt at 282° to be $2·5\times10^{-4}$ and of the solid salt at 282°, $5·8\times10^{-5}$; they also measured the sp. electrical conductivities of soln. of a mol of cæsium,

potassium, ammonium, sodium, and cuprous chloridesin v litres of the molten mercuric chloride at 282°, :

	CsCl		KCl		NH_4Cl		NaCl		CuCl	
v	5	30	2	30	4	15	2	15	2	20
Conductivity .	70·0	44·0	81·0	38·5	70·0	46·5	51·5	28·0	70·0	24·0

H. W. Foote and N. A. Martin consider that complex ions—possibly $MHgCl_4'$ and $NHgCl_5''$—are formed in these soln. The chlorides of the bivalent metals are but sparingly soluble in mercuric chloride. G. Schulze found that, unlike the majority of electrolytes, mercuric chloride at 300° has no influence on the potential of the electrolytic valve-action of tantalum.

Cold sat. soln. of mercuric chloride were found by W. Hampe,[9] M. Faraday, and H. Morse to be poor conductors of electricity. The conductivity of aq. soln. has been measured by O. Grotrian, T. C. Fitzpatrick, H. Ley and H. Kissel, H. C. Jones and K. Ota, L. Kahlenberg, and K. Holdermann. H. Ley found at 25°, with platinized electrodes, for a gram-eq. of the salt in v litres of water :

v . . .	16	32	64	128	256
λ . . .	1·09	1·66	2·55	3·99	6·32

The conductivities are rather less with plain than with platinized-platinum electrodes. H. Arctowsky found that the electrical conductivity of aq. soln. increases perceptibly on standing—presumably because of hydrolysis, and the corresponding formation of hydrochloric acid. E. Rimbach and O. Weber find the conductivity is depressed when lævulose is present in the soln. S. Arrhenius, T. C. Fitzpatrick, L. I. Shaw, W. Hampe, and C. Cattaneo studied soln. of mercuric chloride in ether ; L. Kahlenberg and A. T. Lincoln, H. C. Jones, L. I. Shaw and S. von Laszczynsky, in acetone ; H. Steiner, in methyl acetate ; J. W. Walker and F. M. G. Johnson, in acetamide ; H. D. Gibbs, in methylamine ; J. Kozak and G. Mariasz, in nitromethane ; L. I. Shaw, in epichlorhydrin, acetylchloride, ethyl acetate, benzonitrile, acetic anhydride, salicyl aldehyde, and in aniline. L. I. Shaw failed to confirm the parallelism between the ionizing power and the dielectric constant of these solvents. H. Morse, and W. Hittorf made experiments on the **transport numbers ;** and G. von Elissafoff, on the **electrical endosmose** of aq. soln.

D. Carnegie and F. Burt,[10] and W. Biltz have commented upon the very small **degree of ionization** in aq. soln. of mercuric chloride as revealed by the conductivities, f.p., and b.p. of aq. soln. R. Luther, K. Drucker, M. S. Sherrill calculated the ionization constant K for $Hg''+2Cl'=HgCl_2$ is $[Hg''][Cl']^2=K[HgCl_2]$, from the e.m.f. of the cell $Hg \mid HgCl_2,Hg(NO_3)_2 \mid Hg$, and from the solubility of silver chloride in mercuric nitrate, and the partition of mercuric chloride between toluene and water, and between toluene and mercuric nitrate soln. They find that K is between $1·0\times10^{-14}$ and $1·5\times10^{-14}$. The existence of the ions $HgCl·$ was established by H. N. Morse from the transport numbers, so that the ionization of mercuric chloride $HgCl_2=Hg''+2Cl'$ takes place in stages, $HgCl_2=HgCl·+Cl'$, and $HgCl'=Hg''+Cl'$. The ionization constants for the two last-named processes are $[HgCl·][Cl']=K_1[HgCl_2]$, where $K_1=2·8\times10^{-7}$; and $[Hg''][Cl']=K_2[HgCl·]$, where $K_2=3·5\times10^{-8}$. According to R. Luther, a soln. of mercuric chloride sat. at 25° contains the following constituents, expressed in mols per litre : $[HgCl_2]=0·26$; $[HgCl·]=0·00015$; $[H·]=0·00033$; $[Cl']=0·00048$; $[Hg'']=10^{-8}$; $[HgCl_4'']=5\times10^{-6}$. M. S. Sherrill gives analogous data, and adds that sat. soln. of the mercurous halides have more Hg_2''-ions than the corresponding mercuric halides have Hg''-ions. The equilibrium constants are $[HgCl_4'']=9\times10^{15}[Hg''][Cl']^4$; and $[HgCl_4'']=90[HgCl_2][Cl']^2$. According to S. Arrhenius, the degree of ionization of a $\frac{1}{8}N$-soln. of mercuric chloride when treated with one per cent. by vol. of methyl or ethyl alcohol is changed respectively 0·010 or 0·0112 per cent. R. Salvadori says the salt is more ionized in boiling methyl alcohol than in water or ethyl alcohol. According to F. Röhrs, soln. with a mol of the salt in 6 and in 48 litres of alcohol are ionized respectively 4 and 15 per cent. J. Timmermans has investigated the degree of ionization of soln. in alcohols, aldehydes, ketones, and nitriles.

The older determinations of the **solubility** of mercuric chloride in water were made by G. J. Mulder,[11] J. R. Spielmann, T. Bergmann, A. F. de Fourcroy, J. Davy, and by C. F. Wenzel. More recent determinations have been made by A. B. Poggiale, F. Jander, M. S. Sherrill, H. N. Morse, J. B. Hannay, H. W. Foote and L. H. Levy, A. Étard, and P. Rohland. The data, expressed in grams of salt per 100 grms. of soln., show:

	0°	10°	20°	30°	40°	60°	80°	100°	120°	150°
Per cent. $HgCl_2$	3·5	4·5	5·4	7·2	9·3	14·0	23·1	38	59	78·5

F. Guthrie gives the eutectic or cryohydric temp. as −0·2° when 3·29 per cent. of mercuric chloride is present. From this temp. upwards, the solid phase is $HgCl_2$. No hydrated salts are known, although D. Strömholm compared the solubilities of mercuric chloride in dry and aq. ether, and concluded that *monohydrated mercuric chloride*, $HgCl_2.H_2O$, is formed in ethereal soln., and exists in a state of equilibrium $HgCl_2+H_2O \rightleftharpoons HgCl_2.H_2O$; he also concluded that still higher hydrates may be formed.

The **specific gravities** of soln. of mercuric chloride in various solvents have been measured by O. Grotrian and many others.[12] At 18·5°, C. Bischoff found that for aq. soln.:

Per cent. $HgCl_2$	1	2	3	4	5	6	6·32
Sp. gr.	1·0082	1·0166	1·0252	1·0339	1·0427	1·0512	1·0546

and J. Schröder found the sp. gr. of soln. of various conc. at 0°, 10°, 20°, and 30°. According to J. A. Groshans, at 20°, soln. of sp. gr. 1·0203 and 1·0403 have respectively 2·42 and 4·72 per cent. of mercuric chloride, and the vol. of the solute is 0·430 c.c. and 0·847 c.c. when the mol. vol. are 48·15 and 48·63 respectively. The sp. gr. of soln. in hydrochloric acid have been measured by M. le Blanc and P. Rohland, and R. Engel; in alcohol, by J. Schröder, F. Röhrs, and by W. Herz and F. Kuhn; in acetone, by M. le Blanc and F. Kuhn, and by E. Vogt; in methyl acetate, by F. Bezold, and by A. Naumann and F. Bezold; and in ethyl acetate, by E. Alexander. According to J. Wagner,[13] the **viscosities** of N- and $\frac{1}{8}N$- aq. soln. of mercuric chloride (water unity) are 1·0116 and 1·0042 respectively when the sp. gr. are 1·0275 and 1·0138. J. C. G. de Marignac has measured the velocity of **diffusion** of mercuric chloride in soln. of sodium chloride. F. M. Raoult, E. Beckmann and W. Biltz have found the lowerings of the f.p. of aq. soln. of 0·1867N- and 0·9230N- mercuric chloride to be 0·033 and 0·168 respectively, corresponding with a normal mol. wt. M. le Blanc and A. A. Noyes measured the effect of sodium or potassium chloride in soln. with the mercuric chloride on the f.p., and found evidence of the formation of complexes of the type $KHgCl_3$—*vide infra*. S. Skinner, and W. Landsberger investigated the raising of the b.p. of aq. soln. of mercuric chloride. A. Benrath found that the presence of sodium or potassium chloride in soln. with the mercuric chloride gave results in harmony with the assumption that complex salts are formed. F. M. Raoult has measured the raising of the vap. press.

It has been known for a long time[14] that aq. soln. of mercuric chloride redden litmus; this, says P. Rohland, is due to hydrolytic dissociation yielding an acid with free hydrogen ions which redden litmus, but do not effect methyl orange. From the electrical conductivities, C. Kullgren calculated that for a mol of the salt in v litres of water, the **degree of hydrolytic dissociation** is:

v	8	32	128	512
Hydrolysis at 85·5°	0·60	1·35	2·99	6·91
Hydrolysis at 100°	0·45	1·06	2·31	4·87

The ratios of the two numbers 1·33 is nearly independent of the concentration of the soln. H. Ley suggested that the hydrolysis proceeds either $2HgCl_2+H_2O=(HgCl)_2O+2H^{\cdot}+2Cl'$; or else $HgCl_2+H_2O=HgClOH+H^{\cdot}+Cl'$. L. Kahlenberg's results favour the first hypothesis. The hydrolysis is readily perceptible at 6°; and its amount increases with rise of temp.; H. Arctowsky found that in a sealed tube at 80° the basic product $HgCl_2.3HgO$ is formed, while at 150° a product

$HgCl_2.4HgO$ of higher basicity is formed. From observations with the ultramicroscope at different temp. H. W. Fischer and E. Brieger say that in aq. soln. mercuric chloride is split into hydrochloric acid and a colloid, and that the addition of sodium chloride hinders the hydrolysis by forming Na_2HgCl_4. K. Thümmel, therefore, regards the aq. soln. of mercuric chloride as containing an acid $H_2(HgOCl_2)$ because of the peculiar hydrolytic changes; the solubility of mercuric oxide in soln. of mercuric chloride to form mercuric oxychlorides he regards as evidence pointing in the same direction.

The solubility of mercuric chloride in a great number of solvents has been examined qualitatively or quantitatively. A. C. L. de Bruyn,[15] P. Rohland, M. Centnerszwer, W. Timofejeff, and W. Herz and G. Anders have reported on its solubility in *methyl alcohol* or in mixtures of methyl alcohol and water. According to A. Étard, the percentage solubility in methyl alcohol is:

	−34°	−20°	−2°	4°	12°	36°	62°	100°	127°
Per cent. $HgCl_2$	7·6	11·5	18·7	23·2	27·6	53·1	63·6	68·7	75·2

There is a break in A. Étard's curve at 38°. W. Herz and F. Kuhn find evidence of the formation of an alcoholate, $HgCl_2.CH_3OH$. The percentage solubility in *ethyl alcohol* likewise found by A. Étard is:

	−60°	−55°	−30°	0°	10°	31°	62°	100°	138°
Per cent. $HgCl_2$	3·0	7·8	14·3	29·0	31·3	34·2	42·1	63·6	67·8

According to A. Étard, there are two breaks in this curve, one at −50° and one at 60°. The solubility is augmented by the presence of hydroxylamine hydrochloride. W. Herz and F. Kuhn have measured the solubility in mixtures of methyl and ethyl alcohols. P. Rohland, W. Timofejeff, and A. Étard have measured the solubilities in *propyl alcohol*. A. Étard finds that there is very little increase in the solubility up to 30°; at −32° he says the solubility is 14·7 per cent.; at 0°, 16·4 per cent.; at 41°, 18·2 per cent.; at 67°, 32·7 per cent.; at 100°, 43·8 per cent.; at 127°, 52·7 per cent. W. Herz and F. Kuhn measured the solubility in mixtures of methyl and propyl alcohols, and in ethyl and propyl alcohols. A. Étard gives for the percentage solubility in isobutyl alcohol, at −11°, 5·5 per cent.; at 0°, 6·7 per cent.; at 11°, 7·5 per cent.; at 63°, 19·3 per cent.; at 98°, 32·1 per cent.; and at 155°, 50·4 per cent. According to A. Étard, the solubility in isopropyl alcohol is almost the same as in isobutyl alcohol. A. Étard further gives the percentage solubilities in normal *butyl alcohol*, in *amyl alcohol*, and in *allyl alcohol*:

	n-Butyl alcohol			Amyl alcohol			Allyl alcohol		
	−21°	9°	82°	−13°	26°	106°	−21°	8°	22°
Per cent. $HgCl_2$	12·4	14·3	33·1	8·6	8·9	35·1	20·6	25·2	48·7

The solubility of mercuric chloride in *ether* has been noted by J. Davy, N. E. Henry, and H. P. Madsen. A. Étard found the solubility increases very little with variations of temperature, for it rises from 5·6 per cent. at −47° to 9·0 per cent. at 115°. D. Strömholm found the solubility of mercuric chloride in water is not much affected by the addition of ether; a sat. soln. of ether and mercuric chloride in water dissolves about 10 per cent. less salt than an aq. soln. without ether; on the other hand, the solubility of mercuric chloride in ether rises significantly when water is present. M. J. B. Orfila and J. L. Lassaigne noted that ether extracts mercuric chloride from its aq. soln. The partition of mercuric chloride between ether and water has been measured by A. Hantzsch and F. Sebaldt, F. Mylius and C. Hüttner, D. Strömholm, and S. Skinner. D. Strömholm investigated the effect of additions of acetic acid, ethyl acetate, benzene, chloroform; and F. Mylius and C. Hüttner, the effect of hydrochloric acid on the ethereal soln.

Mercuric chloride dissolves in *acetone*, $CO(CH_3)_2$, forming a heavy colourless liquid. A. Étard measured the solubility over the temp., range −23° to 70°, and noticed that the solubility from 0° to 70° is virtually independent of temp., and A. H. W. Aten found the solubility decreases with rise of temp. above 10°; and, expressing the solubility in mols per cent., he found:

	−15°	0°	10°	10°	17°	25°
Mols of $HgCl_2$	14·5	14·3	18·7	23·5	23·2	22·8
Solid phase	$HgCl_2.(CH_3)_2CO$			$HgCl_2$		

F. Röhrs says that acetone is not a true solvent. The conc. soln., in darkness, changes from red to dark brown—possibly owing to the formation of the compound $HgCl_2.CO(CH_3)_2$; and E. Vogt says that in a few days, the colourless liquid becomes pale yellow without changing its general characteristics. W. Herz and M. Knoch studied the soln. of mercuric chloride in mixtures of acetone and water.

According to O. Aschan and G. Borenius, 95 per cent. *formic acid* dissolves at 19°, 2·1 per cent. of mercuric chloride and 100 c.c. of the soln. have 2·4226 grms. of $HgCl_2$. A. Étard measured the solubility of mercuric chloride in *acetic acid* from which A. Benrath noted that the salt can be crystallized unchanged. According to A. Étard, the solubility rises from 2·7 per cent. at 21° to 8·0 per cent. at 61°, to 12 per cent. at 95°, to 16 per cent. at 115°, to 55 per cent. at 207°. The solubility curve in glacial acetic acid is almost a straight line. A. Étard also found the salt is very sparingly soluble in *propionic acid*, and in *butyric acid*; and that the solubilities of mercuric chloride in *methyl and ethyl formates and acetates* can be represented by almost straight lines. According to A. Étard, at −20°, −3°, 46°, *ethyl formate* dissolves respectively 29·6, 2·92, and 31·0 per cent. of mercuric chloride; at −20°, 24°, and 55°, *methyl acetate* dissolves respectively 42, 40·3, and 41·5 per cent. of mercuric chloride. The solubility in methyl acetate has also been studied by H. Steiner, J. Schröder, F. Bezold and A. Naumann. According to A. Étard, at −50°, 0°, and 19°, *ethyl acetate* dissolves respectively 39·6, 39·5, and 40·2 per cent. of this salt. The solubility in ethyl acetate has also been studied by E. Alexander, M. Hamers, A. Naumann, M. Dukelsky, and A. H. W. Aten. According to C. E. Linebarger, if sodium and mercuric chlorides be present in excess in soln. of ethyl acetate, the compound $NaCl.2HgCl_2$ is formed. M. Hamers, and W. Herz and G. Anders have studied the solubility in aq. soln. of ethyl acetate. According to A. Étard, at 22° and 48°, *amyl acetate* dissolves 18·3 and 18·5 per cent. of mercuric chloride; and at 20°, 55°, and 71°, *ethyl butyrate* dissolves respectively 12·6, 13·5, and 15·1 per cent. J. W. Klever said that mercuric chloride is soluble in *glycerol*; and W. Eidmann, sparingly soluble in *methylal*. G. Glock found that while mercuric chloride is insoluble in *oils* and *fats*, it can be obtained in soln. if it be first dissolved in water-free ketones, or in alcohol-free ether.

According to M. Dukelsky, mercuric chloride is insoluble in *carbon tetrachloride*; but O. Sulc said that at room temp., this solvent dissolves 0·002 grm. M. Dukelsky measured the solubility of mercuric chloride in mixtures of carbon tetrachloride and methyl alcohol. According to M. Dukelsky, at 0° and 45·9°, *ethylene chloride* dissolves respectively 1·33 and 2·42 per cent. of mercuric chloride; and he has studied the solubility of this salt in mixtures of ethylene chloride and methyl alcohol. According to O. Sulc, at room temp. *ethyl bromide* dissolves 2·01 per cent. of mercuric chloride; and *ethylene bromide*, 1·53 per cent. A. Werner said that mercuric chloride is soluble in *methyl sulphide*. M. Dukelsky said that its solubility in *chloroform* is very small, 0·01 and 0·12 per cent. respectively, at −20·5° and 44·2°; for the solubility at room temp., O. Sulc gave 0·106 per cent. A. Hantzsch and F. Sebaldt have studied the partition coeff. of mercuric chloride between water and chloroform; and M. Dukelsky, the solubility of mixtures of chloroform with methyl and ethyl alcohols, and ethyl acetate. At room temp. O. Sulc found that *bromoform* dissolves 0·489 per cent. of mercuric chloride.

According to A. P. M. Franchimont, mercuric chloride is sparingly soluble in cold, but more soluble in hot *benzene*; M. S. Sherrill has also noted the solubility in benzene; and M. Dukelsky found that at 6·5°, 34·1°, and 69·0°, benzene dissolves respectively 0·26, 0·64, and 1·39 per cent. of mercuric chloride; according to W. Timofejeff, the solubility in mixtures of benzene and alcohol at 38°, is greater than that calculated from the solubilities in the two components; M. Dukelsky measured the solubility in mixtures of benzene with alcohol and with ethyl acetate. A. Hantzsch, F. Sebaldt, and A. Vagt, and O. W. Brown measured the partition coeff. of mercuric chloride between *toluene* and water; and H. N. Morse between soln. of mercuric nitrate and toluene. A. Werner said that mercuric chloride is insoluble in *paratoluidine*, and very soluble in aq. *benzonitrile*, and other *aromatic nitriles*. A. Naumann and J. B. Kämmerer say benzonitrile copiously dissolves mercuric chloride with a feeble evolution of heat, forming a clear liquid. L. Mascarelli and M. Ascoli have studied the solubility in *o-nitrotoluidine*, *nitrobenzene*, *p-nitroanisol*, and in *α-nitronaphthalene*, and J. Schröder, and A. Naumann the solubility in *pyridine*. L. Kahlenberg said that mercuric chloride is soluble in *alkyl thiocyanates*. Z. Klemensiewicz found that mercuric chloride is soluble in molten *antimony trichloride*, and that the soln. for great dilutions conduct better than aq. soln.; for conc. soln. aq. soln. are the better conductors. E. H. Büchner said that mercuric chloride is insoluble in liquid *carbon dioxide*; and M. Centnerszwer, that it is insoluble in liquid *cyanogen*. E. Moles and M. Marquina found that the solubility of mercuric chloride is augmented by *glycerol* and *sucrose*, and depressed by *tartaric and citric acids*. The solubility in 100 parts of glycerol at 25° is 80. W. Herz and P. Schuftan measured the distribution of mercuric chloride between water and *tetralin*.

The chemical properties of mercuric chloride.—Mercuric chloride has a sharp metallic taste, and is very poisonous. The powdered salt is stable in **air**, and, according to J. Davy,[16] is not decomposed in **sunlight**; indeed, M. Berthelot found

that the pure salt—dry or moist—is not decomposed in a sealed tube after exposure for a month to sunlight, although pharmaceutical preparations may decompose owing to the presence of reducing agents. O. Wolff could detect no signs of the decomposition of the salt confined in a tube transparent to ultra-violet rays, and exposed to sunlight for a month. In 1803 P. F. G. Boullay reported that the aq. soln. of mercuric chloride is decomposed in sunlight with the formation of mercurous chloride, and the liberation of oxygen and hydrochloric acid. J. Davy made a similar observation in 1822. V. Meyer kept soln. of mercuric chloride in spring water and in highly purified water for two months in darkness, and observed no sign of decomposition, although A. Verda said that the soln. slowly decomposes in darkness with the separation of mercuric oxide, while in light, mercurous chloride is formed. W. van Rijn found a soln. 1 : 5000 decomposed into mercurous chloride and mercuric oxychloride in a few days, and this was attributed to the effect of the cork or of traces of organic matter in the water, or of water on the glass vessel. L. Vignon made similar observations, and stated that the action of the ammonia and dust of the air, and of the products of the action of water on glass, lead to the decomposition of soln. of mercuric chloride exposed to the air. E. Burcker draws the general conclusion that if aq. soln. of mercuric chloride be protected from air and light, they do not change if the solvent be also free from organic and mineral impurities. K. Scheringa found that the effect with the glass of ordinary medicine bottles is only perceptible in a few cases. A. Michaelis says the 1 : 1000 soln. keeps very well in yellow glass bottles, but in blue or white ones it quickly changes. M. Delépine says that mercuric chloride soln. made from spring water with added sodium chloride will keep a week without perceptible change ; and they can be kept longer if the soln. contains enough hydrochloric acid to decompose all the bicarbonates in soln. in the water.

H. Davy (1822) stated that the presence of hydrochloric acid or of ammonium chloride " hinders the decomposition by its affinity for mercuric chloride " ; in the language of the ionic hypothesis the hydrolytic dissociation of mercuric chloride in aq. soln. is hindered by the presence of strongly ionized chlorides. V. Meyer, L. Vignon, E. Burcker, and A. Busch, made the analogous observations that hydrochloric acid, sodium chloride, tartaric acid, and generally, the chlorides or bromides of the alkalies or alkaline earths, hinder the decomposition of soln. of mercuric chloride. L. Vignon also says that the presence of sodium chloride hinders the decomposing action of sodium hydroxide or carbonate, but not very much that of ammonia ; ammonium chloride acts in the reverse way, and both salts make the mercuric chloride soln. more stable in the presence of albumin. R. Bolling, and P. Rohland say that soln. in absolute alcohol are more stable than in water. A. Lesure observed no change after exposing aq. soln. of mercuric chloride to **ultra-violet light** for 15–30 mins. C. Doelter and H. Sirk noted that a one per cent. aq. soln. is coloured yellow after 30 days' exposure to the **radium radiations** from half a gram of radium chloride ; and H. Becquerel found that these radiations reduced mercuric to mercurous chloride in the presence of oxalic acid just as occurs by exposure to light. M. Kofler has also studied the absorption of **radium emanations** by soln. of this salt.

C. D. Zenghelis[17] found that **hydrogen** under ordinary conditions does not reduce a soln. of mercuric chloride, but it does so if the gas is allowed to bubble into the soln. through a filter-paper extraction thimble. H. Moissan noted that **fluorine** attacks mercuric chloride, slowly in the cold, rapidly when heated, forming a yellow fusible fluoride ; and C. Poulenc that it volatilizes in **hydrogen fluoride** gas without decomposition, and it is not altered when fused in **ammonium fluoride.** When heated with **ammonium chloride,** it is not reduced, but a double salt sublimes in needle-like crystals. T. Fairley noted the reduction of mercuric to mercurous chloride by **hypochlorites.** A. Potilizin heated mercuric chloride and **bromine** in a sealed tube, and found 15·16 per cent. of chlorine was expelled. An aq. soln. of bromine, and an ethereal soln. of **iodine,** in light or in darkness, transform mercuric

chloride respectively into mercuric bromide and iodide. According to W. Herz and W. Paul, mercuric chloride soln. dissolve iodine, and this the more the greater the proportion of hydrogen chloride in soln. According to M. C. Schuyten, bromine and iodine displace the chlorine from moist mercuric chloride. F. Gramp found that mercuric chloride is in great part decomposed when heated 6 hrs. with iodine and water in a sealed tube at 250°. According to T. Harth, a soln. of two mols of potassium bromide and one of mercuric chloride gives a mixture of mercuric bromide and potassium chloride quantitatively; but a soln. of two mols of potassium chloride and one of mercuric bromide suffers no change. E. P. Perman said that if mercuric chloride be shaken with **potassium iodide** in the presence of a little moisture, mercuric iodide is formed; in aq. soln. mercuric iodide is precipitated and, according to P. Rohland, in acetone soln., potassium chloride is precipitated. This is a reversal of the behaviour of these salts in aq. soln., and corresponds with the fact that mercuric iodide is far more soluble in acetone than in water, and potassium chloride is less soluble. A series of potassium mercuric iodides are known. V. Borelli was unable to isolate a mixed *mercuric perchloratochloride*, $Cl.Hg.ClO_4$, although he made the corresponding bromo-, chloro-, cyano-, and thiocyano-perchlorates. The presence of a mol of mercuric chloride per mol of perchlorate in soln. raises the electrical conductivity 0·028 per cent., but the addition of another 1·5 mols of the chloride causes no further increase in the conductivity.

A small proportion of **stannous chloride** precipitates mercurous chloride from soln. of mercuric chloride; a larger proportion precipitates mercury as a black powder; according to A. Vogel, some stannic oxide is formed at the same time. According to F. L. Winckler, stannous chloride likewise precipitates mercurous chloride from alcoholic soln. of the mercuric salt. According to J. Bostock, the reaction is so sensitive that one part of mercuric chloride in 500 parts of water is blackened by stannous chloride, and one part of the salt in 20,000 parts of water becomes grey, and gives a precipitate in 24 hrs.; according to P. L. Geiger, the grey colour is perceptible if but one part of mercuric chloride be present in 40,000 parts of water. Stannous chloride precipitates mercurous chloride from soln. in benzonitrile, methyl or ethyl acetate, methylal, and acetone; and from pyridine soln. mercury is precipitated. According to J. L. Proust, a soln. of **cuprous chloride** in hydrochloric acid precipitates mercurous chloride from soln. of mercuric chloride, but L. Gmelin says that the only precipitate so obtained is cuprous chloride. W. von Gulewitsch says a boiling soln. of **aluminium chloride** and mercuric chloride gives a precipitate of mercury and mercuric oxychloride; C. Winther found that when a mixed soln. of **ferrous chloride** and mercuric chloride is exposed to the ultra-violet light of a quartz lamp, mercurous and ferric chlorides are formed; the reaction is slowly reversed in darkness: $HgCl_2+FeCl_2 \rightleftharpoons FeCl_3+HgCl$, but rapidly if it be under conditions where an electric current can be obtained.

The cell was constructed as follows. In a glass funnel, closed at the lower end, a perforated platinum plate was fixed; the plate was soldered to a platinum wire which passed out through a hole in the funnel. On the plate a layer of platinized asbestos was placed and then the soln. which was exposed to the light from a quartz-mercury vapour lamp. After the illumination the differences of potential were measured, a platinum electrode being placed for this purpose in the upper liquid. The e.m.f. in some cases was as much as 0·1 volt, and currents of one milliampère were obtained. Hence, the arrangement has been called a *light accumulator*.

According to H. Schulze,[18] mercuric chloride is not changed when heated in **oxygen** free or nascent. W. D. Bancroft and H. B. Weiser did not get a mirror of mercury on a cold porcelain tube in a Bunsen's flame fed with mercuric chloride, but a white deposit is obtained which is a mixture of mercury and undecomposed salt, along with some black mercurous oxide. G. Tammann found that mercuric chloride accelerates the decomposition of hydrogen peroxide in neutral soln. According to A. Kolb, and M. Kohn, **hydrogen peroxide** reduces mercuric chloride in a neutral or acid soln. provided a neutral tartrate—sodium

potassium tartrate—be present and calomel is quantitatively formed; if heated in alkaline or ammoniacal soln., hydrogen peroxide or sodium peroxide reduces mercuric salts to the metal, a reaction utilized by M. Kohn and A. Ostersetzer for the quantitative determination of mercury in the mercuric halides. According to G. Bredig and W. Reinders, the reduction of mercuric chloride by hydrogen peroxide in neutral soln. is accelerated by colloidal gold or platinum. F. Olivari has shown that the solubility of sulphur or selenium in fused mercuric chloride is not reciprocal in that fused mercuric chloride dissolves **sulphur** or **selenium,** but is not dissolved by them. There is no reaction between mercuric chloride and these two elements at the fusion temp., but with **tellurium** and the fused salt, chemical action occurs to some extent and mercurous chloride is formed: $2HgCl_2+Te \rightleftharpoons Hg_2Cl_2+TeCl_2$. At presumably a higher temp., J. L. Proust found a reaction between mercuric chloride and sulphur, resulting in the formation of mercuric sulphide and sulphur chloride, and he adds that the decomposition may proceed explosively. According to J. Davy, mercuric chloride is not perceptibly attacked by sulphuric acid hot or cold; but, according to H. Rose, A. Vogel, and F. Mohr, when boiled with the acid, there is a very slight formation of mercuric sulphate and the greater part is volatilized unchanged. H. Rose said that mercuric chloride does not absorb the vapours of sulphuric anhydride, but, according to R. J. Kane, in the converse reaction, hydrogen chloride is absorbed with the evolution of heat by mercuric sulphate; and F. Mohr found the reaction: $HgSO_4+2HCl=HgCl_2+H_2SO_4$, is completed at an elevated temp. H. Rose stated that a small proportion of **hydrogen sulphide** precipitates white mercuric sulphochloride, $2HgS.HgCl_2$ or $Hg_3S_2Cl_2$, while an excess precipitates black mercuric sulphide. The **alkali-hydrosulphides** behave similarly. Dry hydrogen sulphide in ether, benzene, ethyl acetate, acetone, pyridine, or benzonitrile soln. of mercuric chloride at first gives a white precipitate which becomes yellow $2HgS.HgCl_2$; in methyl acetate soln., mercuric sulphide is precipitated. Potassium sulphide has no action on soln. of mercuric chloride in benzonitrile; potassium or calcium sulphide likewise has no action with methylal soln. According to J. S. F. Pagenstecher, **metal sulphides**, like freshly precipitated sulphides of zinc, cadmium, lead, tin, copper, antimony, and iron when boiled with mercuric chloride form sulphides and precipitate mercuric sulphochloride: $ZnS+2HgCl_2=ZnCl_2+HgS.HgCl_2$; or $2Sb_2S_5+15HgCl_2=4SbCl_5+5Hg_3S_2Cl_2$. Native sulphides and metallic sulphides prepared in the dry way act slowly, or not at all—*e.g.* zinc blende or native antimony sulphide has no perceptible action. When mercuric chloride is heated in a sealed tube with a little water and lead sulphide, at 160°, A. Levallois observed the transformation: $PbS+HgCl_2=HgS+PbCl_2$.

G. Viard found that an excess of **sulphuric acid** precipitates mercuric chloride from its aq. soln. In general, it may be said that mercuric chloride is fairly easily reduced to mercurous chloride. A. Vogel reported that **sulphurous acid** precipitates mercurous chloride and mercury from an aq. soln. of mercuric chloride; at ordinary temp. very little action is perceptible after 24 hrs., but when heated, the action is rapid. In order to precipitate all the mercury as mercurous chloride a large excess of sulphurous acid frequently renewed is necessary. A mixture of sulphurous acid and mercurous chloride gives no precipitate with an excess of alkalies. W. Sartorius showed that the conc. of the soln. determines the yield of mercurous chloride in the reduction of mercuric chloride by sulphur dioxide. A soln. of mercuric chloride (1 : 80) sat. with sulphur dioxide at 70°–80°, gives a theoretical yield if kept a long time at that temp. A. Sander concluded that the reaction is $2HgCl_2+SO_2+2H_2O=2HgCl+2HCl+H_2SO_4$, and is quantitative when the soln. does not contain over 2 grms. of sulphur dioxide per litre. With greater conc. the gas escapes unoxidized. L. M. Stewart and W. Wardlaw found quantitative reduction occurs when sulphur dioxide reacts at 95° with approximately 2·6 grms. of mercuric chloride in 120 c.c. of water. With a greater conc. of mercuric chloride, reduction is incomplete, and depends on the conc. of hydrochloric acid—*vide* mercurous chloride. According to E. Divers and T. Shimidzu, mercurous chloride is much more soluble in sulphurous

acid than in water; and the soln. on exposure to air rapidly crusts over and deposits a crystalline precipitate of mercuric chloride rendered less soluble by the escape of sulphur dioxide. The addition of sulphuric acid to the soln. of mercuric chloride in sulphurous acid lowers the solubility of the salt and mercuric chloride is precipitated. It is supposed that the soln. of mercuric chloride in sulphurous acid contains **mercuric hydrogen sulphite**: $HgCl_2+2H_2SO_3 \rightleftharpoons 2HCl+Hg(HSO_3)_2$. According to H. Debray, the presence of sodium chloride hinders the reducing action of sulphurous acid. A mercuric chloride soln. can be boiled without reduction if 20 times its weight of sodium chloride be present; but the reduction does occur even then if heated to 120° in sealed tubes. **Ammonium sulphite** has scarcely any action on mercuric chloride soln. in the cold, but if heated, plate-like crystals of mercurous chloride are quickly precipitated, and if the action be allowed to continue, the last-named salt is further reduced and blackened. P. Berthier separated the mercury in globules by warming the blackened mass with hydrochloric acid. According to L. P. de St. Gilles, cold **alkali sulphites** and mercuric chloride soln. form double salts. This accounts for E. Divers and T. Shimidzu's observation that mercuric chloride is much more soluble in a soln. of sodium sulphite or pyrosulphite than in water. N. N. Mittra and N. R. Dhar studied the induced reactions with mercuric chloride and sodium sulphate with sodium arsenite or arsenious acid. When a soln. of **sodium thiosulphate** is added to one of mercuric chloride, T. Poleck and C. Goercki say that no precipitate is at first formed, but the soln. becomes turbid in a few minutes, and later a white precipitate appears which turns yellow and then brown; the dark-coloured precipitate is probably a mixture of mercuric sulphochloride, sulphur, and free mercuric sulphide. According to E. T. Allen and J. L. Crenshaw, if the molar ratio $HgCl_2 : Na_2S_2O_3$ be greater than 3 : 2, white $2HgS.HgCl_2$ is precipitated; if the ratio be 1 : 1 a mixture of this compound with black mercuric sulphide is formed; with a higher proportion of thiosulphate, say 1 : 4, black mercuric sulphide first separates out, a red precipitate of β_1-HgS is formed, and the precipitate forms two layers—the upper red layer is β_1-HgS, and the lower one α_1-HgS. C. R. Wise found that anhydrous **selenium oxychloride** dissolves 0·89 per cent. of mercuric chloride at 25°.

According to J. Davy,[19] 100 parts of hot **nitric acid,** of sp. gr. 1·41, dissolve less than 0·2 part of mercuric chloride. S. Schlesinger says that if the boiling be protracted mercuric nitrate is formed, but this statement does not agree with J. Davy's, P. F. G. Boullay's, or with H. Rose's observations, where the dissolution takes place without decomposition. According to V. Thomas, mercuric chloride is not reduced by heating it with **nitrogen peroxide,** nor, according to J. J. Sudborough, is it changed by **nitrosyl chloride.** The action of **ammonia,** of **hydroxylamine,** and of **hydrazine** is discussed in three special sections—*vide infra*. N. R. Dhar studied the reduction of mercuric chloride with hydrazine hydrochloride and hydroxylamine hydrochloride in the presence of potassium permanganate. Dry ammonia gas in benzonitrile soln. of mercuric chloride gives a white precipitate of $HgCl_2.NH_3$; in pyridine, ethyl acetate, and methylal, a precipitate of $HgCl_2.2NH_3$. According to G. von Knorre and K. Arndt, hydroxylamine is oxidized to nitrous and nitric oxides. H. Davy found that if the vapour of **phosphorus** be passed over heated mercuric chloride, mercury and phosphorous chloride are formed; while if phosphorus be heated with an aq. soln. of mercuric chloride, P. F. G. Boullay found mercury phosphide, phosphoric and hydrochloric acids were produced; and F. Fengler added that phosphorus precipitates mercurous chloride, but no mercury, from an ethereal soln. of mercuric chloride. H. Rose passed **hydrogen phosphide** over warm mercuric chloride, and observed a copious evolution of hydrogen chloride, and the formation of an orange-yellow sublimate of mercuric phosphide which was resolved into its constituents when heated further. H. Rose also found hydrogen phosphide precipitates yellow mercuric phosphochloride, $Hg_3P_2.3HgCl_2.3H_2O$, from aq. soln. of mercuric chloride; and P. Lemoult suggested this soln. as an absorbent for phosphine. A. Bergé and A. Reychler recommended mercuric chloride soln. for removing

phosphine from impure acetylene, but P. Biginelli showed that acetylides are formed by the action of acetylene on mercury chloride. B. Pelletier stated in 1792 that when **tin phosphide** is warmed with a soln. of mercuric chloride, hydrogen phosphide, mercury, and stannic chloride are formed. According to H. Rose, an excess of **hypophosphorous acid** precipitates metallic mercury from soln. of mercuric chloride, while if the mercuric salt be in excess, mercurous chloride is formed—J. R. Thompson obtained mercurous chloride, B. E. Howard the metal. According to H. Rose, **phosphorous acid** precipitates mercurous chloride completely from soln. of mercuric chloride. The reaction is accelerated by heat, and by the presence of nitric or hydrochloric acids. If the mercuric chloride be boiled with an excess of phosphorous acid, the mercurous chloride is grey, and mercury is obtained only in the presence of free acid. The dynamics of the reaction have been studied by C. Montemartini and U. Egidi, by J. B. Garner, J. E. Foglesong, and R. Wilson, and by G. A. Linhart. According to the latter, the reaction proceeds in two stages: $HgCl_2+H_3PO_3=HCl+HgCl+H_2PO_3$, followed by $2H_2PO_3+H_2O=H_3PO_3+H_3PO_4$. The last-named reduction is very fast in comparison with the speed of the former. N. N. Mittra and N. R. Dhar studied the induced reaction between mercuric chloride and sodium phosphite and sodium arsenite or arsenious acid. J. von Liebig noted that soln. of mercuric chloride give no turbidity when mixed with **alkali phosphates,** but after the mixture has stood a long time, a small red deposit appears, and it is rapidly formed with hot soln. K. Haack obtained mercuric oxychloride by the action of **disodium hydrophosphate** on mercuric chloride, and D. Carnegie and F. Burt obtained a dark red precipitate by mixing sat. soln. of **ammonium phosphate** and mercuric chloride. According to L. Amat, **hypophosphoric acid** with cold acid soln. of mercuric chloride furnished a quantitative yield of mercurous chloride. F. Capitaine and N. W. Fischer noted that when **arsenic** and mercuric chloride are heated together arsenic trichloride and a yellowish-brown sublimate of mercuric arsenio-chloride are formed. O. Borrichius found a mixture of **antimony** with one-third its weight of mercuric chloride when pressed into a glass tube becomes hot during the course of half an hour, and when heated forms antimony trichloride and mercury. A similar observation was made by F. Capitaine. N. W. Fischer said that antimony has no action on a soln. of mercuric chloride. **Hydrogen arsenide** was found by H. Rose, and J. Lohmann, to precipitate yellowish or reddish-brown Hg_3AsCl_5. It is supposed that the reaction takes place in stages, first forming yellow chloromercurio arsine, $AsH_2.HgCl$; orange dichloromercurio arsine, $AsH(HgCl)_2$; brown trichloromercurio arsine, $As(HgCl)_3$; and finally black arsenic mercuride, Hg_3As_2. A. Partheil and E. Amort observed similar changes in alcoholic soln. of mercuric chloride chloromercurio arsine, AsH_2HgCl; dichloromercurio arsine, $AsH(HgCl)_2$; and trichloromercurio arsine, $As(HgCl)_3$; each forms arsenious acid, hydrochloric acid, and mercurous chloride in contact with an excess of the mercuric chloride soln. Arsenic mercuride under similar conditions forms mercurous chloride and arsenic, and it is easily decomposed by water, forming arsenious acid, hydrochloric acid, and mercury. G. Franceschi found that arsine precipitates $HAs(HgCl)_2$ from an ethereal soln. of mercuric chloride. According to J. Lohmann, **hydrogen antimonide** at first gives no coloration with a mercuric chloride soln., the soln. then becomes turbid, and a white precipitate is formed; this becomes greyish-white, and consists of mercury and mercurous chloride and possibly some antimony and antimonious oxide. G. Franceschi also found an aq. or alcoholic soln. of mercuric chloride furnishes a precipitate of $HSb(HgCl)_2.3H_2O$ when treated with hydrogen antimonide. H. Rose said that **arsenic oxide** is not altered by mercurous oxide, and K. Haack, that a **disodium hydroarsenate** precipitates mercuric arsenate and mercuric oxychloride. H. Bollenbach found **antimonious oxide** reduces mercuric to mercurous chloride; and F. Rosenthal and J. Severing, that **potassium hexatantalate** gives a precipitate with mercuric chloride.

According to F. W. O. von Coninck,[20] animal charcoal does not effect the decomposition of cold soln. of mercuric chloride. J. L. Gay Lussac and L. J. Thénard

reduced mercuric chloride to mercury by heating it with **carbon,** but, according to J. B. Nevins, mercuric chloride is not reduced by gentle ignition with dry charcoal even if hydrogen be passed over the mixture—the reduction occurs only if the charcoal be moistened; it is reduced if gently ignited with sugar, bread, and the like. The action of **acetylene** on mercuric chloride has been studied by M. Kutscheroff, H. Biltz and co-workers, K. A. Hofmann, P. Biginelli, J. S. S. Brame, B. C. Keiser, etc. A. Bergé and A. Reychler said that acetylene has no action on a soln. of mercuric chloride in dil. hydrochloric acid, and recommended this liquid as a purifying agent for acetylene; but J. S. S. Brame, D. L. Chapman and W. J. Jenkins, and P. Biginelli have shown that the sat. soln. furnishes fine needle-shaped crystals of *chloromercurichloroacetylene*, ClHg.HC : CHCl, after standing some time—*vide* acetylides. G. Gore found that **carbon disulphide** immediately precipitates the sulphide from a soln. of mercuric chloride in ether. N. N. Mittra and N. R. Dhar studied the induced reaction between mercuric chloride and **formic acid** and sodium arsenite. M. Berthelot decomposed dil. soln. of mercuric chloride by **hydrocyanic acid.** H. Rose found **potassium cyanide** first makes the soln. turbid, and this afterwards clears when more cyanide is added, because mercuric chloride and cyanide form soluble complex compounds with mercuric cyanide and the alkali chloride. W. Feld heated mercuric chloride with **potassium ferrocyanide** and obtained mercuric cyanide and mercurous chloride; and H. Rose obtained a white precipitate with soln. of these two salts—the precipitate became blue on standing, and the liquid contained mercuric cyanide in soln. According to K. Schröder, a yellow precipitate of mercuric ferrocyanide is formed, with conc. soln. of potassium ferrocyanide and mercuric chloride. H. Grossmann obtained a crystalline potassium mercuric thiocyanate by mixing conc. soln. of mercuric chloride and **potassium thiocyanate,** but not with dil. soln. Potassium thiocyanate is without visible action on methylal soln. of mercuric chloride; in acetone soln., the first addition of the thiocyanate produces a precipitate which clears up on adding more reagent, with excess, potassium chloride is precipitated; ammonium thiocyanate gives a precipitate of ammonium chloride in acetone and pyridine soln.; in methyl acetate soln., similar results are obtained with potassium and ammonium thiocyanates. H. Moissan and S. Smiles reduced mercuric to mercurous chloride by heating it to 50° or 60° with amorphous **silicon.** According to A. Colson, **silicon sulphide** when heated with mercuric chloride forms silicon chloride $SiCl_4$. O. Ruff and K. Albert found that **silico chloroform** is decomposed catalytically by mercuric chloride at 150°; and M. Phillips, that **copper silicide,** Cu_7Si_2, is decomposed.

J. L. Gay Lussac and L. J. Thénard [21] reported that mercuric chloride is reduced to the metal when heated with **potassium** or **sodium.** S. Kern, and K. Seubert and A. Schmidt found that when mercuric chloride vapour is passed over molten **magnesium,** some mercury is formed which partly amalgamates with the magnesium. According to A. Cossa, **aluminium** reduces the vapour of mercuric chloride with the evolution of heat. According to F. Capitaine, the metals **bismuth, zinc, tin, iron, nickel, lead,** and copper decompose mercuric chloride, forming mercurous chloride or metallic mercury which may form an amalgam with the excess of metal—for example, calomel and stannous and stannic chlorides; and, according to N. W. Fischer, **silver** forms a sublimate of mercurous chloride and a residue of silver chloride. According to N. W. Fischer most metals—nickel, copper, iron zinc, cadmium, bismuth, **platinum, iron,** etc.—precipitate mercurous chloride or mercury or both from aq. soln. Mercury can be completely precipitated by magnesium from aq. soln. of mercuric chloride; H. Rose found that zinc likewise reduces mercury from the same soln. and amalgamation occurs if the soln. is acid; **cadmium** likewise forms needle-like crystals of amalgam. According to S. Peck, iron—*ferrum reductum*—forms mercurous chloride, and N. W. Fischer says that iron precipitates metallic mercury. The reaction is represented $HgCl_2+Fe=FeCl_2+Hg$, and it has been employed for detecting the presence of free iron in the presence of ferrous oxide. According to E. D. Campbell and S. C. Babcock,

mercuric chloride soln. dissolve a little phosphorus and iron in steel, and, according to J. B. J. D. Boussingault, the action is fairly rapid if the iron be suspended by platinum wire. According to R. Varet, nickel produces a little mercury, and mercuric chloride; and, according to M. C. Lea, G. Wetzlar, and A. Vogel finely-divided **silver** forms silver and mercurous chlorides; according to R. Schiff, **palladium** charged with hydrogen reduces mercuric chloride; according to H. Moissan, **chromium** powder is oxidized; and, according to W. C. Reid, **thallium** reduces mercuric salts to mercurous salts and mercury. A. Vogel, M. Caucal, and K. Heumann found that when a strip of **copper** is immersed in a soln. of mercuric chloride, mercury and cuprous chloride are precipitated: $HgCl_2+2Cu=2CuCl+Hg$. If the soln. be acidified with hydrochloric acid, the copper is immediately covered with a white metallic film. H. Reinsch said that no change is perceptible when a strip of copper is immersed in a soln. containing one part of the salt in 5000 parts of water, but if the soln. be boiled, the copper acquires a golden-yellow colour, while if hydrochloric acid be present a grey film appears which, under the microscope, appears to be composed of minute globulets of mercury. The film is visible if but one part of salt is present in 15,000 parts of water. If the copper foil be dried, the grey film when rubbed becomes as bright as silver. Copper, zinc, aluminium, and tin rapidly precipitate mercury and mercurous chloride from soln. of mercuric chloride in benzonitrile; the action is slow with magnesium, iron, antimony, bismuth, nickel, and lead; mercury precipitates mercurous chloride; silver forms a mixed precipitate of silver and mercurous chlorides; arsenic, gold, and platinum have no action. The metals copper, magnesium, zinc, lead, **antimony,** and bismuth precipitate a mixture of mercurous chloride, and mercury from soln. of mercuric chloride in ethyl acetate; mercury and cadmium give mercurous chloride; silver a mixture of mercurous and silver chlorides; iron gives a precipitate of ferrous chloride; nickel, **cobalt, arsenic, gold,** and platinum have no action. Again, zinc, bismuth, and aluminium rapidly precipitate mercurous chloride and mercury from soln. of mercuric chloride in methylal; the action is slow with copper, nickel, magnesium, cadmium, and lead; silver gives a small precipitate of mercury and mercurous chloride; iron and mercury give a precipitate of mercurous chloride; while arsenic, gold, and platinum have no action. Soln. of mercuric chloride in acetone are not reduced by arsenic, antimony, lead, cobalt, and silver; cadmium, copper, nickel, mercury, and tin form mercurous chloride; while magnesium, zinc, iron, aluminium, and bismuth give mercury and mercurous chloride.

H. Rose [22] said a soln. of **ferrous sulphate** does not precipitate mercurous chloride; but ferrous salts generally reduce mercuric salts in darkness; the precipitation of mercurous chloride, according to C. Winther, is hindered by the presence of ferric salts. A. Mailhe said that **nickelous hydroxide** is not affected in the cold, but when heated, some is dissolved. W. Gibbs found mercuric salts were reduced by **ammonium phosphomolybdate.** S. M. Jörgensen found **chloropurpureochromic chloride** and some complex **cobalt salts** give precipitates with mercuric chloride. Mercuric chloride gives a brick-red precipitate of mercurous chromate when treated with soluble normal **chromates,** but not with dichromates.

When dry mercuric chloride is heated with the **alkali hydroxides or carbonates,** a sublimate of mercury and a residue of alkali chloride is formed—in the former case oxygen, and in the latter case carbon dioxide is given off. As C. F. John,[23] and K. Voit have shown, when a hydroxide of the alkalies or alkaline earths is added to a soln. of mercuric chloride, a reddish-brown precipitate of a basic chloride, $Hg_3O_2Cl_2$, or Hg_2OCl_2, is formed provided the mercuric salt be in excess: $2HgCl+2KOH=2KCl+H_2O+HgCl—O—HgCl$; or else $3HgCl_2+4KOH=4KCl+2H_2O+Hg_3O_2Cl_2$; whereas if the alkali be in excess, yellow mercuric oxide is precipitated: $HgCl_2+2KOH=2KCl+H_2O+HgO$. H. Lescœur represents the system as acquiring a state of equilibruim: $HgCl_2+2KOH\rightleftharpoons 2KCl+HgO+H_2O$; and, as shown by M. Lehmann, the basic salts and mercuric oxide are readily soluble in acids. L. Vignon, C. Arnold, W. Herz, and H. Debray have studied the character

of the precipitate produced under different conditions. K. Voit found that if alkali chlorides are present, the soln. can be made alkaline with sodium hydroxide without the formation of a precipitate ; in the presence of ammonium chloride, the precipitate by the alkali hydroxides resembles that produced by aqua ammonia alone. According to L. Dobbin, when a mixture of mercuric chloride with potassium iodide and ammonium chloride is treated with alkali hydroxide, a yellow or brown coloration is produced, but not when treated with alkali carbonate. H. Vittenet found that the **hydrocarbonates** in ordinary water give a small precipitate with a soln. of mercuric and ammonium chlorides. The precipitation is also influenced by the presence of organic compounds—in the presence of conc. acetic acid, for example, A. Vogel found the precipitation is slow and incomplete and with sugar, or gum arabic, lime-water gives no precipitate unless, as F. W. Flashoff and A. W. Buchner showed, the soln. has stood a long time. C. H. Pfaff, and P. L. Geiger found **magnesium oxide** or **calcium oxide** precipitates mercuric oxide, but not, according to A. Mailhe, if alkali chlorides be present. K. Haack said that barium oxide precipitates mercuric oxide from boiling soln. of mercuric chloride. According to A. Naumann, magnesium oxide ; sodium bicarbonate ; calcium oxide, hydroxide or carbonate ; barium, strontium or magnesium carbonate, and potassium hydroxide, are without action on soln. of mercuric chloride in methylal ; potassium carbonate gives a yellow soln. A soln. of mercuric chloride in benzonitrile is coloured yellow, and mercuric carbonate or oxide separates out when the soln. is treated with sodium or potassium hydroxide, and potassium carbonate ; while sodium carbonate or calcium oxide, hydroxide or carbonate has no visible action.

H. Rose,[24] R. Schindler, and C. Winckler, noted that when treated with **alkali carbonates,** a soln. of mercuric chloride first becomes turbid, then reddens, and finally precipitates a reddish-brown basic carbonate, $HgCO_3.3HgO$, that is :

$$O=C<\begin{matrix}O—Hg—O—Hg\\O—Hg—O—Hg\end{matrix}>O$$

Alkali-hydrocarbonates precipitate various oxychlorides from soln. of mercuric chloride. According to H. Arctowsky, **barium carbonate** precipitates a basic salt in the cold with mercuric nitrate but not with the chloride. According to L. L. de Koninck, barium carbonate usually acts only on those salts which can be more or less decomposed hydrolytically by water so as to form a basic salt and free acid. The barium carbonate acts by neutralizing the free acid and leaves the water still further to react with the salt. P. L. Geiger also found an excess of **magnesium carbonate** gives a reddish-yellow precipitate with soln. of mercuric chloride. According to K. Thümmel, ammonium carbonate soln. give a yellow precipitate of an ammine oxychloride, $HgCl_2.HgO.2NH_2HgCl$. According to M. Dukelsky, the **borates** of the alkalies and alkaline earths, magnesia, and magnesium hydroxide or carbonate give a precipitate of mercuric oxychloride, but not of mercuric oxide.

According to F. Diacon,[25] soln. in **alcohol** reduce mercuric to mercurous chloride, and the action is faster the greater the number of hydroxyl groups in the mol., for example, **mannite** is carbonized at 140°. According to J. Davy, and P. F. G. Boullay, the soln. in aq. alcohol—not absolute alcohol or ether—is reduced to mercurous chloride in sunlight, while a soln. in turpentine oil is not affected by light. E. Feider found **aldehydes**—*e.g.* **formaldehyde**—reduce mercuric chloride soln. to mercury. According to P. A. von Bonsdorff, **potassium formate** at 50°–80° reduces mercuric to mercurous chloride, and with protracted boiling mercury is formed ; and, according to J. W. Döbereiner, and F. L. Winckler, a boiling soln. of **sodium formate** reduces mercuric to mercurous chloride, but not to mercury. The reaction was proposed to M. Portes and M. Ruyssen, as a method for the quantitative determination of the formates and formic acid, but A. Scala showed that the reaction is not quantitative in the presence of acetic and butyric acids ; and A. Lieben, that a large excess of mercuric chloride is needed, and the mixture must be heated 6–8 hrs. on a water-bath. H. Rose showed that the presence of various

chlorides or of acetic acid retards the speed of the reduction. A. Findlay and M. J. P. Davies showed that the reaction is of the second order, and the velocity determinations agree with: $2HgCl_2+H.COONa=2HgCl+NaCl+HCl+CO_2$; and it is therefore inferred that the reduction takes place in stages. G. A. Linhart and co-workers explain the reduction by the same hypothesis as that employed for the reduction with phosphorous acid—*q.v.* N. R. Dhar said that the oxidation of sodium formate is unimolecular with respect to both substances, and the whole reaction is bimolecular. When exposed to light, mercuric chloride is reduced by **oxalic acid** or the **alkali oxalates** to mercurous chloride—with **ammonium oxalate,** ammonium chloride and carbon dioxide are formed at the same time. The sat. soln. do not react in darkness. The reduction by ammonium oxalate is faster in vacuo, or in an atm. free from oxygen. N. R. Dhar showed that the reaction $2HgCl_2+K_2C_2O_4=2KCl+2CO_2+2HgCl$ is induced by sunlight, the light from a carbon arc, a quartz mercury vapour lamp, or an arc between electrodes of thoria and zirconia. A. Jodlbauer and H. von Tappeiner said that the reaction is accelerated by fluorescent substances—fluorescein, anthracene, anthraquinone disulphonate, acridine, benzoflavine, phenylquinaldine, quinine, æsculine, and by hydrogen; and J. H. Kastle and W. A. Beatty say that it is accelerated by 0·000000,0195 grm. of potassium permanganate, by 0·000000,016 grm. of ferric chloride, or by other oxidizing agents, but slackened by potassium chromate. N. R. Dhar studied the reduction of mercuric chloride with oxalic, **tartaric, malic, malonic, glycollic, and citric acids**. Malonic acid acts more slowly than oxalic acid. According to E. Rupp and A. B. Dott, tartaric acid reduces mercuric chloride in the presence of manganese dioxide; **potassium tartrate** reduces mercuric to mercuric chloride in darkness and in light; the reaction is accelerated by heat. The white of an egg or **albumin** gives a white sparingly soluble precipitate with mercuric chloride, and hence its use as an antidote for corrosive sublimate. J. B. Kämmerer [26] found that between 30° and 40° the white of an egg also reduces some mercuric to mercurous chloride. J. Müller found the presence of sodium chloride retards the precipitation. According to T. Gayda, the thermal value of the reaction is 14·3 cals. per grm. of albumin, and is independent of the vol. of the soln. According to M. Siegfried, a soln. of **gelatine** gives a precipitate with a soln. of mercuric chloride, and the filtrate furnishes crystals of mercurous chloride after standing for some time, and **glycocoll** behaves similarly, precipitating crystals of mercurous chloride in about ten days. J. B. Nevins says an aq. soln. of one part of corrosive sublimate and 160 parts of **gum arabic** becomes turbid in a few hours, and in 6 days furnishes a small grey deposit, and he obtained analogous results with decoctions of various plants. F. Vulpius found **pepsin** also reduced mercuric to mercurous chloride. A. Vogel, and H. Ley, said that **sugar** precipitates mercurous chloride from a boiling soln. of mercuric chloride. Many organic compounds form addition compounds with mercuric chloride and a very great number of organo-mercury compounds have been reported. Mercuric chloride is one of the best of antiseptics, and it is used in aq. soln. 1 : 1000 or 1 : 4000. It enters into the composition of a number of medicinal preparations.

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§ 13. Mercuric Oxychlorides—Basic Mercuric Chlorides

The hydrolytic action of water on aq. soln. of mercuric chloride has been previously discussed. In 1815, J. L. Proust [1] showed that some mercuric oxide dissolves when boiled with aq. soln. of mercuric chloride; the soln. becomes turbid on cooling, and deposits crystals of a mercuric oxychloride. In 1849, C. Roucher emphasized the fact that the composition of the oxychloride formed by the action of mercuric chloride soln. on mercuric oxide is different according as the yellow or red oxide is used, and likewise according to the temp. and nature of the solvent. A large number of mercuric oxychlorides—and in some cases isomeric forms—has been reported. They are produced by the action of red or yellow mercuric oxide on aq. or alcoholic soln. of mercuric chloride; by the incomplete precipitation of a soln. of the chloride by an alkali hydroxide, carbonate, or bicarbonate; by fusing together the oxide and chloride at about 300°; by the incomplete action of chlorine on mercuric oxide; or by the hydrolytic action of water on oxychlorides of low basicity. Nine compounds with $HgCl_2 : HgO$ respectively as 2 : 1, 1 : 1, 2 : 3, 4 : 7, 1 : 2, 1 : 3, 1 : 4, 1 : 5, and 1 : 6 have been reported, and for some of these isomeric forms have been described. A. Driot said that the four oxychlorides 2 : 1, 1 : 1, 1 : 2, and 1 : 3 exist in soln. when mercuric oxide is boiled with an aq. soln. of mercuric chloride for eight hours—when 0·5 to 4·0 per cent. of the last-named salt is present, the 1 : 3 compound separates in yellow to black needles when the soln. cools; with 4·0 to 8·0 per cent. $HgCl_2$, black rhombohedra of the 1 : 2 salt; with 30 per cent. $HgCl_2$, a mixture of the 1 : 2 and 1 : 3 salts which can be separated by levigation from the 2 : 1 salt. He also prepared the 1 : 1 salt as indicated below. A. Driot made only one form of each of the four oxychlorides. K. Thümmel believed that only the five compounds 2 : 1, 1 : 1, 1 : 2, 1 : 3, and 1 : 4 really exist. E. P. Schoch omitted the 1 : 1 compound, and further supposed that isomeric forms of the 1 : 2, 1 : 3, and 1 : 4 forms exist. As in the case of the other basic chlorides, there is some uncertainty as to which of the oxychlorides are chemical individuals, and the uncertainty will remain until the conditions of stability have been thoroughly investigated in the light of the phase rule. S. Toda studied the system H_2O-$HgCl_2$-HgO, at 35°, and the results are summarized in Fig. 14, where N denotes $100m/(100+m)$ in the ratios $100mH_2O : xHgCl_2 : (100-x)HgO$. Here there are only two oxychlorides 1 : 1, and 1 : 4. E. P. Schoch proposed naming the oxychlorides in such a way as to indicate by a numerical prefix the number of mercury and oxygen atoms in the simplified empirical formula. This is a temporary expedient until the constitution and mol. wts. are known.

C. Roucher prepared yellow cubic crystals of the 1 : 2 salt, **trimercuric oxychloride,** $HgCl_2.2HgO$, or ClHg.O.Hg.O.HgCl, by dissolving as much finely divided mercuric oxide as possible in a boiling soln. of 30 to 35 grms. of mercuric chloride in 100 c.c. of water. The crystals which separate between 60° and 70° are dried, and then washed with ether. K. Thümmel, E. P. Schoch, and A. Driot employed somewhat similar processes. Indeed, according to the former, this compound is present in all soln. of mercuric chloride in which mercuric oxide has been dissolved,

and he added that if a conc. soln. of mercuric chloride be carefully poured over moist mercuric oxide at the bottom of a tall cylinder, white octahedral crystals of the 2 : 1 salt will grow above the black 1 : 2 salt. According to K. Thümmel, the crystals have a sp. gr. 6·42 (27·5°). The salt is decomposed by warm water or cold alcohol, forming the red 1 : 2 salt; and with hot alcohol, the black 1 : 2 salt is formed. According to C. Roucher, potassium hydroxide gives a yellow precipitate, and, according to K. Thümmel, sodium hydroxide gives a red precipitate of mercuric oxide. N. Tarugi failed to prepare this salt according to C. Roucher's or K. Thümmel's directions, for the chlorine in the product he obtained varied between 16 and 21 per cent., and never came near the theoretical 18·7 per cent. required for the 2 : 1 salt; but E. P. Schoch's products gave 18·4 to 18·56 per cent. of chlorine. S. Toda obtained no evidence of this compound at 25°.

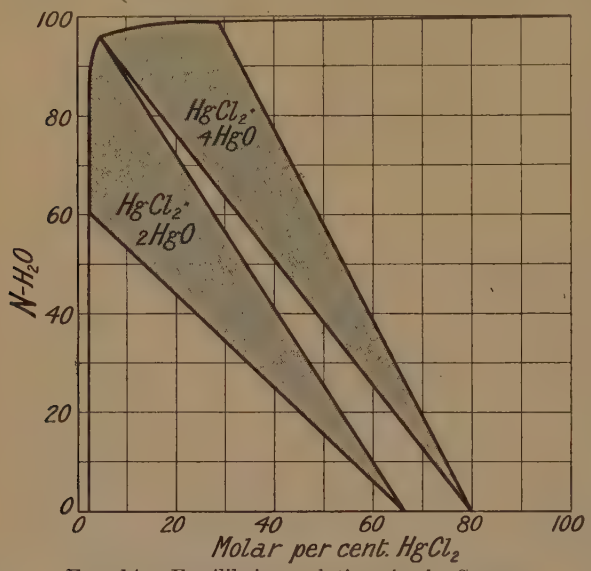

FIG. 14.—Equilibrium relations in the System $HgCl_2$—HgO—H_2O, at 35°.

A. Driot prepared a yellow amorphous powder of the 1 : 1 salt, **dimercuric oxychloride,** $HgCl_2.HgO$, that is, HgCl—O—HgCl, by heating mercuric oxide for six days at 100° with an excess of a 30 per cent. soln. of mercuric chloride; or by the evaporation of a sat. soln. of mercuric oxide in mercuric chloride on a water-bath, and washing out the free mercuric chloride with alcohol. G. André says this salt cannot be obtained in the wet way, and he made it by heating 0·1 eq. of red mercuric oxide with rather more than 0·1 eq. of mercuric chloride in a sealed tube in an oil-bath. K. Haack made it as a yellow precipitate by mixing dil. or conc. soln. of mercuric chloride and disodium hydrogen phosphate in any proportion whatever; and he also made it by adding powdered mercuric chloride to molten disodium hydrogen phosphate. According to G. André, the heat of formation (HgO, $HgCl_2$) is 1·65 Cals. The salt gives yellow mercuric oxide when treated with potassium hydroxide. K. Thümmel supposed this salt existed in an aq. soln. of mercuric oxide in mercuric chloride, but he did not succeed in its isolation; he suggested that it might be regarded as the mercuric salt of the hypothetical acid, $H_2(OHgCl_2)$, namely, $Hg(OHgCl_2)$. S. Toda obtained this compound under the conditions indicated in Fig. 14. He said that it furnishes dark purple-red acicular crystals, and is probably the compound made by J. Volhard from mercuric chloride and sodium acetate, and by N. A. E. Millon, K. Thümmel, and E. P. Schoch from mercuric chloride and potassium carbonate.

The 2 : 3 salt was reported by G. André to be formed as an amorphous precipitate when a soln. of yellow mercuric oxide in a hot sat. soln. of magnesium chloride is cooled and then poured into a large excess of water. K. Voit made what he regarded as the 4 : 7 salt by gradually adding aq. sodium hydroxide to a dil. soln. of mercuric chloride—with the first addition, the soln. remains clear, then it becomes opalescent, and deposits a white flocculent precipitate which becomes yellow and then red on exposure to air. A soln. of sodium chloride restores the white colour. The white flocculent precipitate, dried at 100°, has a composition corresponding with $4HgCl_2.7HgO$.

If mercuric oxide be mixed with a 30 per cent. soln. of mercuric chloride, and kept for six days at 100°, the 1 : 1 salt is formed ; but with a 4–8 per cent. soln. of the chloride, black rhombohedral crystals of the 1 : 2 salt appear ; and if a 0·5 to 4 per cent. soln. of the chloride is used, yellow to black needle-like crystals of the 1 : 3 salt are formed. If the oxide be heated with the chloride in a sealed tube, the 1 : 2 salt appears. Red and black forms of the 1 : 2 salt, **trimercuric dioxychloride,** $HgCl_2.2HgO$, have been reported. According to E. P. Schoch, the methods for preparing the two varieties are analogous except that for the black the liquid should be alkaline, and acid for the red. The *red variety* seems to have been first made by A. J. Balard by the action of calcium hypochlorite on mercury. N. A. E. Millon made it by the action of a cold sat. soln. of potassium bicarbonate on 6 to 10 times its volume of a soln. of mercuric chloride, sat. at 15°. G. André used a similar method. There are several modifications of N. A. E. Millon's process for making this salt, by adding a soln. of a normal or acid alkali carbonate to one of mercuric chloride : *e.g.*, for each mol proportion of mercuric chloride, K. Thümmel used 1·375 of $KHCO_3$, 0·667 to 2·0 of $NaHCO_3$, or 0·1 to 0·167 of Na_2CO_3 in a boiling soln. The mother liquid should be promptly poured off the red precipitate or the colour changes to purple, violet or brown. E. P. Schoch heated an intimate mixture of mercuric oxide with half a mol. proportion of mercuric chloride for 6 to 8 hrs. in a sealed tube at 300°, and extracted the mass with anhydrous ether in Soxhlet's apparatus so as to remove the free mercuric chloride. If less mercuric chloride be used a mixture of the 1 : 2 and the 1 : 4 salts is formed. K. Haack made this salt by the action of disodium hydrogen phosphate on a soln. of mercuric chloride. H. Arctowsky heated in a large flask to 90° for 48 hrs. a 5 per cent. soln. of mercuric chloride with some pieces of marble. After removing the marble, the soln. was cooled slowly to 50° for the salt.

When an excess of mercuric oxide stands in contact with a dil. soln. of mercuric chloride, the *black variety* of trimercuric dioxychloride forms in the lower layers where the influence of the mercuric oxide is predominant ; it does not form in the upper layers. According to P. C. Ray, if a neutral soln. of mercurous nitrite, which is always contaminated with a little mercuric nitrite be treated with sodium chloride, mercurous chloride is precipitated, and if an excess of the salt soln. be used, the spontaneous evaporation of the filtrate furnishes a mixture of two oxychlorides of the same composition, $HgCl_2.2HgO.\frac{1}{2}H_2O$, but one is black, the other orange. Sodium hydroxide converts the black variety into the orange-coloured one. The black variety was made by M. Donovan, and P. Grouvelle by the action of red mercuric oxide on a soln. of mercuric chloride ; R. Phillips, K. Thümmel, E. P. Schoch, and A. Driot used a similar process. Thus, the last-named boiled a 4 to 8 per cent. soln. of mercuric chloride, sat. with mercuric oxide, for about 8 hrs., and filtered the hot liquid. On cooling the compound separated out. C. Roucher made it by the action of alcoholic soln. of mercuric chloride on mercuric oxide. H. Thaulow treated mercuric oxide with cold chlorine hydrate, or hypochlorous acid. J. Volhard made it by mixing a cold sat. soln. of mercuric chloride and sodium acetate. The liquid is alkaline, and after standing some days, crystals of the black compound appear along with a flocculent substance which is easily separated. A further crop of crystals is obtained by adding some potassium hydrocarbonate. J. S. van Nest hung a piece of marble in a 5 per cent. soln. of mercuric chloride heated on a water-bath for 48 hrs. at 70° ; and slowly cooled the liquid. K. Thümmel treated 10 parts of dry trimercuric dioxynitrate, $Hg(NO_3)_2.2HgO.H_2O$, for 3 hrs. with a soln. of 1·9 parts of potassium chloride ; the precipitate which is at first red changes to black. N. A. E. Millon made the black 1 : 2 salt by pouring one vol. of a cold sat. aq. soln. of potassium bicarbonate into three vols. of a soln. of mercuric chloride sat. at 15°, and on stirring with a glass rod black streaks appeared on the walls of the beaker. The liquid is poured from the beaker and a new mixture run in, and stirred. The precipitate which forms is washed with cold water, and dried over sulphuric acid. E. P. Schoch used an analogous process.

The red variety is coloured various shades of red, and, according to E. P. Schoch, it forms pyramidal crystals belonging to the hexagonal system, while, according to J. Blaas, the black variety, obtained by the prolonged action of dil. nitric acid on partially precipitated mercuric chloride, forms monoclinic prismatic crystals which, according to J. Volhard, have the axial ratios $a:b:c=0{\cdot}9178:1:0{\cdot}9978$, and $\beta=65°\ 30'$. J. S. van Nest gave rather different measurements for a sample prepared by the calcium carbonate process—*viz.* $a:b:c=1{\cdot}9728:1:1{\cdot}0452$, $\beta=125°\ 57'$. E. P. Schoch gave for the sp. gr. of the red variety 8·16 to 8·43 (27·5°); and for the black variety, 8·53; for the black variety also J. Volhard gives 8·670 (17°); J. S. van Nest, 8·286; and J. Blaas, 8·63, and hardness 2·5. Neither compound is affected by water at ordinary temp. Potassium or sodium hydroxide gives yellow mercuric oxide with the red variety; and red mercuric oxide with the black variety. Alkali carbonates and chlorides readily attack the red variety in the cold, but not the black variety even on boiling. According to M. C. Lea, the red variety is darkened by the application of a high press. G. André gives the heat of formation ($HgCl_2$, $2HgO$) as 3·15 Cals. N. Tarugi believes that both varieties are only mixtures because of the variability in the analyses of different preparations. S. Toda obtained no evidence of the existence of this compound in his study of the ternary system $HgCl_2$—HgO—H_2O, at 35°.

According to W. F. Hillebrand and W. T. Schaller, the mineral *kleinite* from Terlingua (Texas) has the composition 85·86 per cent. Hg; 7·30 per cent. Cl; 3·10 per cent. SO_4; 2·57 per cent. N; and 1·03 per cent. H_2O, and it is thought to be a mixture of a mercury ammonium chloride, NHg_2Cl, with a smaller amount of mercury sulphate or oxysulphate. A. Sachs' analyses of a mineral from Breslau corresponded with the formula for **tetramercuric trioxychloride,** $HgCl_2.3HgO$, and he regarded the nitrogen and sulphuric acid, also present, *als Beimengung nicht als integrirende Bestandtheile des Minerals*. W. F. Hillebrand also found minute octahedral crystals of *mosesite*, a canary-yellow mineral analogous in composition and properties to kleinite, on calcite from Terlingua (Texas). The crystals of kleinite are hexagonal with $a:c=1:1{\cdot}6642$. The sp. gr. of the orange crystals of kleinite is 7·96 to 7·99 and of the yellow crystals 7·94 to 8·04. The hardness is between 3 and 4. The crystals of kleinite and mosesite are optically birefringent, but they become isotropic respectively at 194° and 184°; on cooling, they slowly revert to the birefringent form. The mean refractive index of kleinite is 1·8. The crystals of mosesite are slowly changed to calomel by hydrochloric acid; kleinite is slowly dissolved. There is no perceptible sublimate when kleinite is heated to 260°, for many hours, but between 260° and 280°, a sublimate of calomel and mercury appears.

Tetramercuric trioxychloride, $HgCl_2.3HgO$, has been reported in yellow crystals of prismatic and tabular habits, as a yellow and as a brick-red amorphous powder. E. P. Schoch made *yellow prismatic crystals* of $HgCl_2.3HgO$ by shaking together for ten minutes a mixture of freshly precipitated mercuric oxide with a cold sat. soln. of mercuric chloride in proportions not exceeding two mols of the latter to one of the former. After decanting off the liquid, the residue was dried on a porous tile, and washed with absolute ether. If ordinary powdered and levigated yellow or red mercuric oxide be employed, as recommended by K. Thümmel, the product agrees with $HgCl_2.3HgO$, containing much free oxide. A. Driot made the same compound by saturating with mercuric oxide a boiling soln. with between 0·5 and 4 per cent. of mercuric chloride. After boiling 8 hrs. the mixture was filtered rapidly and the crystals of $HgCl_2HgO$ which first separate are followed by those of the salt in question. These are washed with alcohol. N. A. E. Millon made *yellow tabular crystals* by pouring a cold soln. of mercuric chloride, sat. at 15°, into an equal volume of a sat. soln. of potassium bicarbonate; G. André employed an analogous process; he mixed equal volumes of cold sat. soln. of mercuric chloride and potassium bicarbonate; J. S. van Nest poured soln. of mercuric chloride and potassium bicarbonate in the mol. proportion 8 : 11 into about a litre of water at 85°. H. Arctowsky heated two

litres of a 5 per cent. soln. of mercuric chloride for a month at 80°, and cooled the soln. every evening; if the temp. be 97° he said the compound is not formed. C. Roucher reported citron-yellow amorphous powders to be formed by the action of mercuric oxide on a soln. of mercuric chloride, but K. Thümmel says it is a mistake to suppose these powders amorphous, they are crystalline. P. Grouvelle, K. Voit, N. A. E. Millon, and G. André have also described brick-red amorphous powders obtained by the action of alkali hydroxides or carbonates, or calcium chloride on mercuric chloride. K. Haack made them by the action of a soln. of sodium chloride on mercuric phosphate, or a mixture of mercuric and an alkali chloride. The red powder probably differs from the yellow, merely in the size of grain.

N. Tarugi suggested that all these processes for preparing the compound $HgCl_2.3HgO$ give mixtures of mercuric oxide and chloride in indefinite proportions because instead of the theoretical 7·72 per cent. of chlorine, the yellow crystalline substance prepared in different ways contained from 3·8 to 7·9 per cent. of chlorine; the yellow amorphous powder, 2·9 to 6·2 per cent. of chlorine; and the brick-red powder 3·6 to 8·1 per cent. of chlorine. He added that he prepared small yellow crystals of definite composition by placing small cubes of white statuary marble of a sugar-like texture in a sat. soln. of mercuric chloride at 15°; the crystals which were formed in 15 to 20 days were separated, washed in hot water, and dried in vacuo. This process is analogous to that employed by R. Phillips in 1830. According to E. P. Schoch, the yellow prisms have a sp. gr. 7·93 (27·5°). The compound is not changed by light, by heating to 110°, or by boiling with a 7 per cent. soln. of mercuric chloride; with an excess of mercuric chloride it forms $2HgCl_2.HgO$. According to E. P. Schoch, when heated with water it forms yellow plates of $HgCl_2.4HgO$; and, according to K. Thümmel, alkali carbonates and chlorides also transform it into the 1 : 4 salt; boiling with mercuric oxide does the same thing; and alcohol decomposes it, forming mercurous chloride. According to G. André, the heat of formation of the yellow plates is ($HgCl_2$, 3HgO), 3·95 Cals. N. Tarugi said that when heated, or boiled with water or alkali soln., this oxychloride is decomposed into its constituents, while dil. nitric acid converts it into a white amorphous powder. S. Toda obtained no evidence of this compound in his study of the ternary system $HgCl_2$—HgO—H_2O, at 35°.

A. F. de Fourcroy and L. J. Thénard obtained a precipitate by adding a small amount of potassium hydroxide to a soln. of mercuric chloride, and, according to G. André, the product when dried at 100° is an amorphous brown powder of **penta-mercuric tetraoxychloride,** $HgCl_2.4HgO$. K. Thümmel made the same product by treating a sat. soln. of mercuric chloride with normal or acid alkali carbonate—say one mol of $HgCl_2$ with 30 to 35 of $KHCO_3$. N. A. E. Millon also made this product by boiling the amorphous 1 : 2 or 1 : 3 salts with water. The crystalline variety is made, according to H. Arctowsky, by heating 2 litres of a 5 per cent. soln. of mercuric chloride for a month at 100° allowing the soln. to cool in the evening; the yield is 25 per cent. He also made the same crystals by leaving pieces of marble in a 10 per cent. soln. of mercuric chloride at 39° for three months. G. André made it by heating for 7 hrs. to near the b.p. red mercuric oxide with four times as much mercuric chloride in aq. soln.—analogous methods were employed by E. P. Schoch, H. Thaulow, and K. Thümmel. According to E. Soubeiran, if an excess of an alkali carbonate soln. be added to a soln. of mercuric chloride, a red precipitate is formed, and nearly all the mercury is removed from the soln.; but if insufficient alkali carbonate be added to precipitate all the mercury, the red powder at first precipitated changes to brown crystals. If the soln. of mercuric chloride be previously mixed with sodium chloride so as to produce a less easily decomposable double salt, a white turbidity first appears on the addition of the alkali carbonate, and the brown crystals eventually separate. The formation of these crystals is accelerated by heat since the excess of carbon dioxide is expelled from the alkali carbonate and its decomposing action on the mercuric chloride prevented; but if the temp. exceeds 40°, the precipitate will be mixed with free mercuric oxide.

K. Thümmel, N. A. E. Millon, and J. S. van Nest used analogous modes of preparation. M. Dukelsky and J. S. van Nest substituted a dil. soln. of borax for the alkali carbonate. K. Thümmel also made the same crystalline product by the action of potassium bicarbonate on the crystalline 1 : 1, 1 : 2, or 1 : 3 salt; and N. A. E. Millon obtained it by the action of water on the two last-named salts. S. Toda studied the conditions of formation of this compound, Fig. 14, and it appeared as a brownish-yellow substance, amorphous to the naked eye. According to E. P. Schoch, this salt forms hexagonal plates, reddish-brown or black in colour, and of sp. gr. 8·008 to 8·170 at 27·5°. G. André says the heat of formation of all varieties ($HgCl_2.4HgO$) is 9·86 Cals. According to N. A. E. Millon and K. Thümmel, alkali hydroxides give red mercuric oxide; alkali bicarbonates have no action; it is soluble in acids, insoluble in alcohol and ether. There are some differences in the reports of the composition of the black shining crystals; for instance, O. B. Kühn gave $2HgCl_2.5HgO$; H. Thaulow, $HgCl_2.4HgO$; and P. Grouvelle, $HgCl_2.5HgO$. According to N. Tarugi, identical products cannot be obtained by any of the given methods of preparation, for they have a variable composition, and cannot therefore be chemical individuals.

C. Roucher and K. Thümmel have reported the 1 : 5 salt, *hexamercuric pentoxychloride*, $HgCl_2.5HgO$, by allowing a soln. of mercuric chloride to stand in contact with mercuric oxide; and the 1 : 6 salt, *heptamercuric hexa-oxychloride*, $HgCl_2.6HgO$, by the action of an excess of mercuric oxide on cold mercuric chloride dissolved in water frequently renewed, form $HgCl_2.6HgO.H_2O$; but, by using a larger quantity of chloride, the anhydrous salt is produced. Neither of these basic chlorides is so well-defined as those which precede, and S. Toda obtained no evidence of their existence in his study of the system $HgCl_2$—HgO—H_2O, at 35°; but the oxychloride 1 : 4 forms solid soln. with mercuric oxide.

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§ 14. Mercuric Ammino-chlorides

Amidogen, NH_2, can combine with the metals. The metal amides have a remarkable tendency to unite with the chlorides or oxides of the same metal or a metal of the same family to form compounds which resemble the oxychlorides, sulphochlorides, or oxysulphides. . . . Ammonia, NH_3, that is, hydrogen amide, $H.NH_2$, can play the same part as water, hydrogen oxide, either as basic water or as water of crystallization. It can equally well replace the water to which T. Graham applied the term saline water.—R. J. Kane (1839).

In addition to the *double salts* of mercury and ammonium which are analogous with the double salts of mercury with salts of potassium and the other basic metals,

there is a series of *ammino-compounds* [1] in which ammonia, NH_3, plays the part of the water of crystallization in the salts of mercury; another series of *ammonio-basic salts* in which amminolysis analogous with hydrolysis has occurred, and which is typified by the reaction: $HgCl_2+2NH_3 \rightleftharpoons NH_2.Hg.Cl+NH_4Cl$, analogous with $HgCl_2+H_2O \rightleftharpoons HO.Hg.Cl+HCl$. Just as the hydrolysis of the chlorides is retarded by hydrochloric acid so is their amminolysis retarded by the presence of ammonium chloride. There is still another series of mixed *aquobasic salts* or ammino-basic salts in which both amminolysis and hydrolysis have occurred, and it may be typified by the amminolytic reaction: $HgCl_2+2NH_3 \rightleftharpoons NH_2.HgCl+NH_4Cl$, followed by the hydrolytic reaction: $2(NH_2.Hg.Cl)+H_2O \rightleftharpoons NH_4Cl+ClHg.NH.HgOH$.

G. Gore,[2] E. C. Franklin and C. A. Kraus, and F. M. G. Johnson and N. T. M. Wilsmore find mercuric chloride to be soluble in *liquid ammonia;* the two unite to form a series of addition products—ammino-chlorides—in which the ammonia behaves in an analogous manner to water in salts containing water of crystallization. Similarly, H. D. Gibbs said that mercuric chloride unites with liquid *methylamine*, forming a white addition product which is but sparingly soluble. According to P. Grouvelle (1821), and H. Rose (1830), ammonia gas is slowly absorbed by mercuric chloride at ordinary temp.—5·75 per cent. in two days—the absorption is more rapid if the salt be warmed, and if melted and then cooled in this gas, the salt takes up 6·8 per cent. of ammonia. The product thus corresponds with mercuric monammino-chloride, $HgCl_2.NH_3$. The six ammino-salts of mercuric chloride which have been reported have the ratio $HgCl_2 : NH_3$ as 1 : 1, 2 : 3, 1 : 2, 1 : 3, 1 : 4, and 1 : 12. The 3 : 2 salt—**trimercuric diamminochloride,** $3HgCl_2.2NH_3$—reported by D. Strömholm, as a product of the action of ammonia on an almost sat. soln. of mercuric chloride in ether, is generally regarded as a mixture. It was, however, prepared by M. C. C. Holmes by a digesting at 100° infusible precipitate in a soln. of 47 grms. of ammonium chloride and 65–130 grms. of mercuric chloride. The crystals obtained on cooling the filtered soln. were washed twice with alcohol, twice in ether, and left in vacuo for some hours.

The product of the action of a current of ammonia gas on heated mercuric chloride, or that obtained by volatilizing a mixture of mercuric oxide and ammonium chloride, was supposed by R. J. Kane to be **mercuric monamminochloride,** $HgCl_2.NH_3$—*vide supra.* E. Mitscherlich [3] prepared the same compound by sublimation from a mixture of mercuric oxide and ammonium chloride; and G. André, by the gradual addition of a soln. of mercuric chloride to an ammoniacal soln. of ammonium chloride so as to avoid a rise of temp. The curdy precipitate is washed by decantation with cold water until it loses the smell of ammonia, and then dried at 100°. A. Naumann made it by passing an excess of ammonia gas into a soln. of mercuric chloride in benzonitrile. This compound melts when heated, and sublimes without much loss of ammonia; it is insoluble in water, but is decomposed by prolonged contact with hot water, forming a yellow substance. According to R. J. Kane, it is resolved by water into soluble alembroth salt and insoluble infusible white precipitate: $2(HgCl_2.NH_3)=NH_2.Hg.Cl+NH_4HgCl_3$. L. Pesci believed the alleged monoammine to be most probably a mixture.

R. Varet claims to have made *mercuric sesquiammino-chloride,* $2HgCl_2.3NH_3$, by the action of ammonia gas at 0° on mercuric chlorocyanide, HgClCy; R. Jarry also supposed this compound to be present in ammoniacal soln. of mercuric chloride.

There have been many attempts to explain the composition of *fusible white precipitate* or the white precipitate—*mercurius præcipitatus albus*—of the pharmacopœia, and the systematic name applied to the compound has changed with the fashion for representing its composition in a particular way. Thus, its ultimate composition corresponds with $HgCl_2.2NH_3$, and C. F. Rammelsberg,[4] and L. Pesci arranged the symbols to $3NH_4Cl.NHg_2Cl$, which makes it appear as a double *ammonium dimercuriammonium chloride.* H. Gaudech on arranged the symbols $2HCl.NHg_2(NH_3)_3Cl$; K. A. Hofmann and E. C. Marburg, $Hg(NH_3Cl)_2$,

mercuridiammonium chloride; and H. Fürth, $NH_3Cl.Hg.NH_3Cl$, or else as $Cl.Hg.NH_3Cl$. According to E. C. Franklin, it may be formulated as $HgCl_2.2NH_3$, or $Hg(NH_3)_2Cl_2$, where the ammonia is united as ammonia of crystallization. This latter view makes the name **mercuric diammino-chloride.**

Mercuric diammino-chloride was made by E. Mitscherlich by slowly adding a soln. of mercuric chloride to a boiling ammoniacal soln. of ammonium chloride so long as the precipitate redissolves; the rhombohedral crystals of the salt—possibly contaminated with a little infusible white precipitate, $NH_2.Hg.Cl$—separate out on cooling. D. Strömholm used an analogous process. C. F. Rammelsberg made this salt by dissolving freshly precipitated mercuric oxide in an ammonium chloride soln. and treating the liquid with aqua ammonia. G. André, H. Gaudechon, and K. A. Hofmann and E. C. Marburg employed an analogous process. According to G. André, the curdy precipitate can be obtained in a crystalline form by heating with ammonia to 200° in a sealed tube. P. L. Geiger has stated that a cold soln. of ammonium chloride has no action on red mercuric oxide, but that a hot soln. the colour of the red oxide changes to yellow, provided that the soln. contains approximately one part of ammonium chloride for every four parts of mercuric oxide; while if about one part of ammonium chloride is present for every two parts of oxide, infusible white precipitate is formed; and, added L. Gmelin, fusible white precipitate is produced if an excess of ammonium chloride be present. P. Geiseler made this compound by adding sodium or potassium carbonate, in not too great an excess, to a cold aq. soln. of equal parts of mercuric and ammonium chlorides—every 100 parts of the mercuric chloride required 191 parts of crystallized sodium carbonate for complete precipitation, and yielded 103·2 parts of the well-dried precipitate—1·4 parts of mercury remained in soln. If about $3\frac{1}{2}$ times as much sodium carbonate be used for the precipitation, the precipitate when washed acquires a yellow tinge, but recovers its whiteness when washed with a soln. of sal-ammoniac. A. Duflos, G. Krug, K. Thümmel, and C. H. Hirzel obtained similar results with ammonium carbonate. L. Pesci, C. F. Rammelsberg, G. Krug, and R. J. Kane converted mercuric amidochloride, $NH_2.Hg.Cl$; dimercuriammonium chloride, NHg_2Cl; and the chloride of Millon's base, $HO.Hg.NH.Hg.Cl$, into mercuric diammino-chloride by treatment with a soln. of ammonium chloride. According to E. Vogt, and A. Naumann, mercuric diammino-chloride is precipitated when dry ammonia is passed into a cold soln. of mercuric chloride in acetone; in pyridine (J. Schröder); in ethyl acetate (A. Naumann, M. Hamers, and E. Alexander); in methyl acetate (F. Bezold); and in methylal (W. Eidmann).

Mercuric diammino-chloride forms small rhombohedral crystals. According to A. Duflos, the precipitate is not altered by heating it to 135°; it gives ammonia and a white sublimate at 180°; and at 300°, it fuses to a clear colourless liquid which, according to F. Wöhler, gives off nitrogen and ammonia and then sublimes. The sublimate when treated with water leaves a residue of mercurous chloride, and a soln. of mercuric and ammonium chlorides. According to G. Krug and K. Vahle, if the heating be stopped when the evolution of ammonia has ceased, the molten mass congeals to a reddish-brown fibrous mass. According to E. Alexander, when heated in a sealed tube, ammonia is first evolved, and mercuric chloride sublimes. Mercuric diammino-chloride is stable in water only in the presence of a great excess of ammonium chloride, and when treated with water, it is first converted into fusible white precipitate: $HgCl_2.2NH_3 \rightleftharpoons NH_2.Hg.Cl + NH_4Cl$, and finally, after long washing into the chloride of Millon's base: $2(NH_2.Hg.Cl) + H_2O \rightleftharpoons HO.Hg.NH.Hg.Cl + NH_4Cl$, and hence H. Gaudechon says that boiling water decomposes it into ammonia and mercuric chloride; R. J. Kane, into the yellow compound the chloride of Millon's base, $NH_2.Hg.O.Hg.Cl$, or $HO.Hg.NH.Hg.Cl$. The last stage of the reaction is: $HO.Hg.NH.Hg.Cl + H_2O \rightleftharpoons 2HgO + NH_4Cl$. The reactions are reversible, and hence the action of water on mercuric diamino-chloride can be reversed, for by digesting mercuric oxide with ammonium chloride, the chloride of Millon's base, $HO.Hg.NH.Hg.Cl$, is first formed; then infusible white precipitate, $NH_2.Hg.Cl$;

and finally, $HgCl_2.2NH_3$. According to F. A. Flückiger, and C. H. Hirzel iodine converts mercuric diammino-chloride into mercurous and mercuric chlorides, mercuric iodide, nitrogen, and ammonia : $2I_2+6Hg(NH_3)_2Cl_2=N_2+6NH_4Cl+4NH_3+2HgCl_2+2HgI_2+2HgCl$. Mercuric diammino-chloride is readily dissolved by acids; and K. Dieterich says if it has been dried below 30° it is soluble in cold dil. acetic acid, and if dried above 30°, insoluble. According to K. A. Hofmann and E. C. Marburg, 10 per cent. nitric acid, sulphuric acid, and acetic acid form a clear soln. of mercuric chloride and the ammonium salt. According to T. Weyl, a cold soln. of potassium hydroxide is without action, but H. Gaudechon says that in the cold an excess of the lye gives off three-fourths of the nitrogen, as ammonia ; when the mixture is heated, ammonia is evolved ; and L. Pesci, K. A. Hofmann and E. C. Marburg say that all the nitrogen may be driven off as ammonia by boiling the salt with potash-lye. L. Pesci also says that when distilled with sodium carbonate, three-fourths of the nitrogen is given off as ammonia ; silver nitrate precipitates the chlorine completely ; H. Fürth said that ethyl iodide in the absence of water forms primary ethylamine ; and M. Zipkin, and E. Schmidt and L. Krauss said that methyl iodide—cold or hot, with or without methyl alcohol—gave tetramethyl-ammonium mercuric iodide : $N(CH_3)_4I.HgI_2$.

T. Weyl prepared white crystals of a compound with the empirical composition $HgCl_2.2NH_3$ by dissolving mercuric chloride in liquid ammonia, and volatilizing the excess of ammonia. Unlike the preceding compound, however, T. Weyl's product gives off ammonia when treated in the cold with potash-lye, and it forms a yellow product—thought to be chloride of Millon's base, HO.Hg.NH.Hg.Cl. G. André reported an ill-defined hydrated form of mercuric diammino-chloride.

R. Varet obtained a precipitate of **mercuric triammino-chloride,** $HgCl_2.3NH_3$, by the action of a soln. of dry ammonia in absolute alcohol upon dry mercuric chlorocyanide, HgCyCl. The compound is rapidly altered on exposure to air, and is decomposed by water. With aqua ammonia and mercuric chlorocyanide, infusible white precipitate, $NH_2.Hg.Cl$, is formed ; and with dry ammonia gas at 70°, a greyish-white complex, $4HgCyCl.3NH_3$, is formed. A. Naumann and J. B. Kämmerer passed dry ammonia into a half-sat. soln. of mercuric chloride in benzonitrile ; and after the liquid was sat. with the gas, pressed the precipitate to free it from mother liquid. It was thought to be **mercuric tetrammino-chloride,** $HgCl_2.4NH_3$. E. C. Franklin and C. A. Kraus prepared **mercuric dodecamminochloride,** $HgCl_2.12NH_3$, by dissolving mercuric chloride in liquid ammonia. The compound is stable only under press. ; it solidifies at a low temp., and melts at —9°.

K. A. Hofmann and E. C. Marburg[5] prepared **mercuric hydrazino-chloride,** $HgCl_2.N_2H_4$, by the action of hydrazine hydrate on an alcoholic or ethereal soln. of mercuric chloride. It is stable when dry. It decomposes with a hissing noise when heated, but it does not explode ; it readily dissolves in mineral acids, and the soln. deposits some mercurous chloride. There is evidence of a decomposition analogous with the hydrolytic and amminolytic decomposition of mercuric amminochloride in contact with water : $2Hg(N_2H_4)Cl=N_2H_4.2HCl+Cl.Hg.NH.NH.Hg.Cl$. M. Adams has reported **mercuric dihydroxylamino-chloride,** $HgCl_2.2NH_2OH$, or $Hg(NH_2OH)_2Cl_2$, to be formed in needle-like crystals by mixing gradually at —10° cold alcoholic soln. of the component salts. The hydrazine and hydroxylamine in these compounds probably function in the same way as ammonia in the ammino-compounds and as water of crystallization in hydrated salts.

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§ 15. Double and Complex Salts of Mercuric Chloride—The Chloromercuriates

H. Rose [1] found that mercuric chloride is more readily soluble in hydrochloric acid than in water, and, as J. Davy showed in 1822, heat is developed during the reaction. The solubility of mercuric chloride in aq. soln. of hydrochloric acid has been measured by M. le Blanc and A. A. Noyes, by R. Engel, and by A. Ditte. According to R. Engel, at 0°, 100 c.c. of the soln. contain:

Grms. HCl .	1·57	3·61	6·49	9·81	12·48	15·13	17·54	25·84
Grms. $HgCl_2$.	13·11	18·04	32·44	49·04	62·40	75·65	87·70	129·20
Sp. gr. . .	1·117	1·238	1·427	1·665	1·874	2·023	2·066	2·198

M. S. Sherrill calculated the ratio of the mol. conc. of hydrogen chloride to the increase in the solubility of mercuric chloride from A. Ditte's data at 16°, and found a rise from 1·0 to 3·3. This was attributed to the formation of complex ions, of the type $HgCl_5''$. A. Ditte has reported hydrated forms of the $HgCl_2$: HCl=3 : 1; 2 : 1; 3 : 4; and 1 : 2 salts.

In 1822, J. Davy obtained a mass of needle-like crystals, which, according to P. F. G. Boullay's analysis, consist of **hydrotrichloromercuric acid,** $HgCl_2.HCl$, or $HHgCl_3$, by cooling a soln. with molecular proportions of the two components, $HgCl_2$: HCl=1·2, using an acid of sp. gr. 1·158. G. Neumann made the same salt by sat. a. soln. of hydrochloric acid with mercuric chloride at the ordinary temp. of a room, and evaporating the liquid in a desiccator over sulphuric acid and quicklime at the temp. of a winter's cold, −0° to −4°. The heat of the reaction, according to R. Varet, is 0·86 Cal. J. Davy said that the crystals lose hydrogen chloride (and water) when heated, leaving mercuric chloride as a residue; they melt by the heat of the hand; and, according to G. Neumann, are decomposed by moisture. A. Ditte obtained white plates of **hydroheptachlorotrimercuric acid,** $3HgCl_2.HCl$, or HHg_3Cl_7, by crystallizing a sat. soln. of mercuric chloride in hydrochloric acid

over 80°; if the crystallization takes place at about 60°, needle-like crystals of $3HgCl_2.HCl.5H_2O$ are formed. P. F. G. Boullay (1827), and A. Ditte (1881) made prismatic crystals of **hydropentachlorodimercuric acid,** $2HgCl_2.HCl.4\frac{1}{2}H_2O$ and $2HgCl_2.HCl.6H_2O$—the former from a soln. sat. at 30°, and allowed to stand at 20°; the latter, by passing hydrogen chloride into a soln. in presence of an excess of mercuric chloride at 15°. The liquid, cooled by cold water, deposits, on standing, crystals which can be dried in an atm. of hydrogen chloride. M. le Blanc and A. A. Noyes say that **hydrotetrachloromercuric acid,** H_2HgCl_4, must be formed in soln. because the f.p. of dil. hydrochloric acid is raised by additions of mercuric chloride and then again depressed with further additions of the salt. The electrical conductivity of hydrochloric acid also is decreased by the addition of mercuric chloride; sodium chloride behaves similarly, but potassium chloride does not since it forms a sparingly soluble double salt. G. Neumann obtained crystals of the salt $HgCl_2.2HCl$ by cooling a soln. of the components in these proportions to −12°. R. Varet gives 0·80 Cal. for the heat of formation. A. Ditte obtained crystals of **hydrotetrachloromercuric acid,** $HgCl_2.2HCl.7H_2O$, by saturating a hydrochloric acid soln. of mercuric chloride at −15°, and at −10° passing a current of hydrogen chloride. The crystals are dried on a porous tile at −5°. By working at 5° instead of −10°, A. Ditte claimed to have made crystals of **hydrodecachlorotrimercuric acid,** $3HgCl_2.4HCl.14H_2O$. It is not yet clear which of these substances is a mixture and which a true compound. C. R. Crymble says that when hydrochloric acid is added to a $\frac{1}{10}N$-alcoholic soln. of mercuric chloride, the absorption increases up to a maximum with equimolar proportions of HCl and $HgCl_2$, and he says that the presence of higher complexes than $HgCl_2.HCl$ cannot be proved in soln.

Y. Shibata, T. Inouye, and Y. Nakatsuka observed that soln. of complex salts extend their absorption bands towards the ultra-violet zone more than do the component salts. With this criterion, they inferred that mercuric chloride forms complex salts with the chlorides of hydrogen, ammonium, sodium, potassium, magnesium, zinc, cadmium, calcium, strontium, barium, manganese, cobalt, nickel, aluminium, zirconium, and tin; with the bromides of ammonium, sodium, potassium, zinc, and cobalt; and with the iodides of cadmium.

Mercuric chloride is readily soluble in water containing ammonium chloride in soln. At 15·6° J. Davy found 100 parts of a sat. soln. of ammonium chloride dissolve almost an equal weight (99·56) of mercuric chloride. About the time of Paracelsus, a compound of sal ammoniac with corrosive sublimate was prepared by crystallization from a soln. of mercuric chloride with an excess of ammonium chloride, and employed medicinally by the iatrochemists under the name *sal sapientiæ*—the *salt of wisdom*—or *sal alembroth*—*ἄμβροτος*, immortal, gold-like, divine. G. C. Wittstein [2] made it by boiling a soln. of ammonium chloride with mercuric or mercurous oxide or carbonate—with the mercurous compounds some metal separates out. The heat developed on mixing soln. of ammonium and mercuric chlorides has been studied by R. Varet—$(HgCl_{2aq.}, NH_4Cl_{aq.})=0·54$ Cal., $(HgCl_{2aq.}, 2NH_4Cl_{aq.})=0·98$ Cal.—the lowering of the f.p., by F. M. Raoult, and by H. C. Jones and N. Knight; and the electrical conductivity, by H. C. Jones and K. Ota. According to R. Schindler and F. L. Winckler, the soln. containing a mixture of equal parts of mercuric and ammonium chlorides gives a white precipitate with the alkali carbonates or hydroxides; with water containing calcium carbonate in soln.; and sugar precipitates calomel from hot soln. (87°), but not from cold soln. Alembroth salt is probably a mixture of ammonium chloride with $HgCl_2.2NH_4Cl.H_2O$. J. D. Holmes reported the salts $(NH_4)_2Hg_9Cl_{20}$ and $(NH_4)_2Hg_3Cl_8.4H_2O$, but gave no satisfactory evidence in support of their chemical individuality.

As E. Soubeiran [3] showed in 1827, when a soln. containing equal parts of ammonium and mercuric chlorides is evaporated and cooled, a crop of crystals of ammonium chloride first separates in cubic crystals, often twinned; these are followed by the rhombic pyramids or needle-like crystals of the compound **monohydrated ammonium tetrachloromercuriate,** $HgCl_2.2NH_4Cl.H_2O$, or $(NH_4)_2HgCl_4.H_2O$.

E. Soubeiran said that the crystals of the latter salt were to be mechanically picked out from those of the ammonium chloride, and purified by recrystallization. P. A. Meerburg's work at 30° shows that these crystals are alone obtained from soln. with between 21·4 and 24·3 per cent. of ammonium chloride and 50·6 and 56·0 per cent. of mercuric chloride with respectively 24·79 and 50·05 per cent. of ammonium and mercuric chloride, a mixture of ammonium chloride and $HgCl_2.2NH_4Cl.H_2O$ is formed at 30°; and with respectively 20·06 and 58·97 per cent. of ammonium and mercuric chloride, a mixture of $HgCl_2.2NH_4Cl.H_2O$ and $HgCl_2.NH_4Cl.H_2O$ separates out at 30°. According to A. Johnsen, the rhombic crystals have the axial ratios $a:b:c=0{\cdot}7120:1:0{\cdot}7725$, and sp. gr. 2·84; J. Grailich says they have a strong positive double refraction. C. F. Rammelsberg said the crystals are isomorphous with those of potassium tetrachloromercuriate, $K_2HgCl_4.H_2O$. H. Töpsöe made an analogous series of substituted ammonium compounds: *e.g.*

$[NH_3(CH_3)]_2HgCl_4$	monoclinic	$a:b:c=0{\cdot}6030:1:0{\cdot}8488$, β 96° 20′
$[NH_3(C_2H_5)]_2HgCl_4$	tetragonal	$a:c=1:0{\cdot}9243$
$[NH_2(C_2H_5)_2]_2HgCl_4$	monoclinic	$a:b:c=0{\cdot}6515:1:0{\cdot}4555$, β 94° 56′
$[NH(CH_3)_3]_2HgCl_4$	monoclinic	$a:b:c=0{\cdot}7033:1:0{\cdot}4698$, β 92° 3′
$[NH(C_2H_5)_3]_2HgCl_4$	hexagonal	$a:c=1:0{\cdot}8451$
$[N(CH_3)_4]_2HgCl_4$	rhombic	$a:b:c=0{\cdot}3766:1:0{\cdot}7893$
$[N(CH_3)_3(C_2H_5)]_2HgCl_4$	rhombic	$a:b:c=0{\cdot}7263:1:0{\cdot}8458$
$[N(CH_3)_2(C_2H_5)_2]_2HgCl_4$	rhombic	$a:b:c=0{\cdot}7660:1:0{\cdot}8660$
$[N(CH_3)(C_2H_5)_3]_2HgCl_4$	tetragonal	$a:c=1:0737$
$[N(C_2H_5)_4]_2HgCl_4$	tetragonal	$a:c=1:1{\cdot}2190$

According to E. Soubeiran, the crystals of hydrated ammonium tetrachloromercuriate are stable in air; they become opaque at 40°; and lose 5·5 per cent. of water. They decompose when heated and a mixture containing ammonium and mercuric chlorides is obtained as a sublimate. The crystals are almost perfectly miscible with boiling water, but at 10°, the solubility is 40 per cent. When a little hydrogen sulphide is passed into the soln. a white precipitate is formed; with more of the gas, the precipitate blackens; sodium or potassium hydroxide gives a white precipitate and ammonia gas is evolved; aqua ammonia, says C. H. Hirzel, gives a white precipitate, but E. Soubeiran said that no precipitate is formed; the latter added that sulphuric, hydrochloric, or nitric acid produces no visible change. According to C. H. Hirzel, crystals containing a lower ratio than $HgCl_2:NH_4Cl=1:2$ cannot be obtained. J. M. Thomson and W. P. Bloxam reported the separation of crystals of the trihydrated salt, $HgCl_2.2NH_4Cl.3H_2O$, by seeding a supersaturated soln. with prismatic crystals of mercuric chloride precipitated from hot soln., but P. A. Meerburg did not find these crystals.

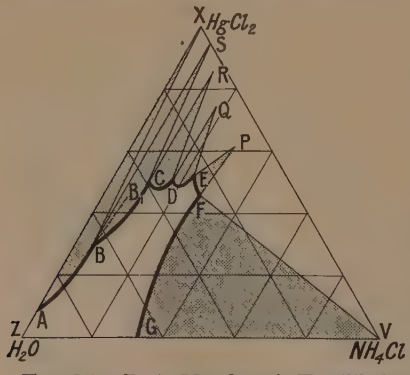

Fig. 15.—P. A. Meerburg's Equilibrium Diagram for the Ternary System, $HgCl_2-NH_4Cl-H_2O$.

At least nine salts have been reported—taking the order $HgCl_2-NH_4Cl-H_2O$; these are 5.1.0; *9.2.0; 2.1.0; 3.2.0; *3.2.1; *1.1.0; *1.1.1; *1.2.1; and 1.2.3. The five marked with an asterisk were alone found by P. A. Meerburg to be stable in aq. soln. at 30°. P. A. Meerburg applied the principles of the phase rule to the ternary system, $HgCl_2-NH_4Cl-H_2O$, at 30°, and the results are summarized in the diagram, Fig. 15, which shows the composition of the soln. The points *X*, *Y*, *Z* respectively denote the components $HgCl_2$, NH_4Cl, and H_2O; *P* represents the solid phase $HgCl_2.2NH_4Cl.H_2O$; *Q*, $HgCl_2.NH_4Cl.H_2O$; *R*, $3HgCl_2.2NH_4Cl.H_2O$; and *S*, $9HgCl_2.2NH_4Cl$. The isothermal line *ABCDEFG* has six branches showing the composition of the soln. in stable

equilibrium with the solid phases—*AB* with $HgCl_2$; *BC*, with 9.2.0; *CD*, with 3.2.1; *DE*, with 1 : 1 : 1; *EF*, with 1.2.1; and *FG*, with NH_4Cl. The line *AB* may extend to B_1 indicating that the solid phase, $HgCl_2$, is then in a metastable condition, and passes more or less quickly into the 9.2.0 phase. This solid phase is voluminous and cryptocrystalline. The line *AB* represents the composition of soln. in equilibrium with the solid phase $9HgCl_2.2NH_4Cl$; *CD*, with $3HgCl_2.2NH_4Cl.H_2O$; *DE*, with $HgCl_2.NH_4Cl.H_2O$; *EF*, with $HgCl_2.2NH_4Cl.H_2O$; and *FG*, with NH_4Cl. Soln. represented by points inside the sectors deposit the solid phase represented by the corresponding equilibrium line. Soln. represented by points on *B*, *C*, *D*, *E*, and *F*, are in equilibrium with two solid phases. The point *G* represents the solubility of ammonium chloride in water; *A* that of mercuric chloride.

J. Davy prepared crystals of what he regarded as a double salt, $HgCl_2.NH_4Cl$—that is, **ammonium trichloromercuriate,** NH_4HgCl_3—by sublimation from a mixture of equimolar parts of the two components; D. Strömhold says this compound is the end-product of the extraction of the higher mercuric ammonium chlorides, say, $9HgCl_2.2NH_4Cl$; and H. Edhem-Bey made it by treating mercuric amidochloride, NH_2HgCl, with chloroform and allowing the mixture to stand in light or shaking every now and again during 5 weeks. The soln. is then evaporated. R. J. Kane says he obtained the salt by crystallization from an aq. soln. of its components, but P. A. Meerburg failed to find any evidence of the existence of this salt in aq. soln. at 30°, so that R. J. Kane's product was probably **monohydrated ammonium trichloromercuriate,** $NH_4HgCl_3.H_2O$, since P. A. Meerburg has shown that at 30° this hydrated product separates from aq. soln. with between 18·86 and 56·83 per cent. respectively of ammonium and mercuric chlorides, and 14·22 and 56·71 per cent. of the same two chlorides; with soln. containing 19·98 and 58·89 per cent. respectively of ammonium and mercuric chlorides, a mixture of the 2.1.1 and 1.1.1 salts is formed; and with 14·10 and 57·04 per cent. respectively of the same two salts, a mixture of the 1.1.1 and 3.2.1 salts is formed. R. J. Kane also made the monohydrated salt, and E. Mitscherlich said that it is isomorphous with the corresponding potassium salt. J. Davy says the anhydrous salt melts readily, and forms a greyish-white crystalline mass on cooling. C. Tourneux also made the monohydrate.

J. D. Holmes prepared needle-like crystals of a form of **ammonium octochlorotrimercuriate,** $3HgCl_2.2NH_4Cl$, with 7 per cent. of combined water, which it loses when dried at 100°. P. A. Meerburg has shown that the monohydrated salt, $2NH_4Cl.3HgCl_2.H_2O$, and not the anhydrous salt, is formed at 30° in aq. soln. with between 13·90 and 56·83 per cent. respectively of ammonium and mercuric chlorides and between 9·23 and 58·55 per cent. respectively of the same two salts. A soln. with 14·14 and 56·98 per cent. respectively of ammonium and mercuric chlorides gives a mixture of the 1.1.1 and the 3.2.1 salts; and a soln. with 9·20 and 58·65 per cent. respectively of the same two salts gives a mixture of the 3.2.1 and the 9.2.0 salts. D. Strömholm made this salt by evaporating a hydrochloric acid soln. with three mols of mercuric chloride to one of ammonium chloride. The soln. is cooled when crystallization begins, and the crystals are dried by press. They lose a mol of water when dried in a desiccator or at 60°. J. D. Holmes also reported a tetrahydrated salt, $3HgCl_2.2NH_4Cl$, in needle-like crystals by evaporating a soln. of the component salts with a great excess of hydrochloric acid—however this may be, the salt does not exist in aq. soln. at 30°.

J. D. Holmes also obtained triclinic crystals of **ammonium eicosichloroenneamercuriate,** $9HgCl_2.2NH_4Cl$, that is, $(NH_4)_2Hg_9Cl_{20}$, by cooling a hot aq. soln. of one part of ammonium chloride and 25 parts of mercuric chloride acidified with hydrochloric acid. P. A. Meerburg found that the salt is formed in soln. at 30° with between 8·76 and 51·83 per cent. respectively of ammonium and mercuric chlorides, and 5·06 and 32·90 per cent. respectively of the same two salts. A soln. with 9·20 and 58·65 per cent. respectively of ammonium and mercuric chlorides gives a mixture of the 3.2.1 and 9.2.0 salts, and a soln. with 3·62 and 29·65 per cent.

respectively of the same two salts, a mixture of the 9.2.0 and 1.0.0 salts. According to J. D. Holmes, the sp. gr. of the salt is 3·06. The presence of free hydrochloric acid seems to retard the decomposition of this salt by water. When potassium hydroxide is added to the soln. a yellow precipitate is obtained which gives no ammonia gas even when boiled; the soln. gives a yellow precipitate with an excess of platinous chloride. P. C. Ray reported the formation of white crystals of **ammonium pentachloro-dimercuriate,** $2HgCl_2.NH_4Cl$, *i.e.* $NH_4Hg_2Cl_5$, by evaporating a soln. of dimercuriammonium nitrite, $NHg_2NO_2.\frac{1}{2}H_2O$, in warm dil. hydrochloric acid. The salt fuses and sublimes at a gentle heat, and is very soluble in water. D. Strömholm also reported the formation of rhombohedral crystals of **ammonium henicosichloropentamercuriate,** $5HgCl_2.NH_4Cl$, or $NH_4Hg_5Cl_{21}$, by a process analogous with that employed by J. D. Holmes for the 9.2.0 salt, and although H. L. Wells suggested that J. D. Holmes's 9 : 2 : 0 salt is really the 5 : 1 : 0 salt, P. A. Meerburg's work shows that the converse is the more probable, and D. Strömholm's, that the 5 : 1 : 0 salt is really the 9 : 2 : 0 salt. As indicated by T. Curtius and F. Schrader,[4] hydrazine hydrochloride, like ammonium chloride, forms double salts with mercuric chloride. K. A. Hofmann and E. C. Marburg obtained crystals of **hydrazine trichloromercuriate,** $(N_2H_5)HgCl_3$, *i.e.* $HgCl_2.N_2H_5Cl$, melting at 157°, by the action of a soln. of chlorine in carbon tetrachloride on a soln. of mercurous hydrazinochloride, $2HgCl.N_2H_4$, in the same solvent, and by re-crystallization from boiling alcohol. They also made it from the component salts with the mercuric chloride in excess. K. A. Hofmann and E. C. Marburg made **dihydrazine tetrachloromercuriate,** $(N_2H_5)_2HgCl_4$, *i.e.* $HgCl_2.2N_2H_5Cl$, by evaporating to dryness an aq. soln. of 2·1 grms. of $N_2H_4.2HCl$ and 3 grms. of mercuric chloride, acidified with hydrochloric acid; the excess of mercuric chloride was extracted from the powdered mass by cold absolute alcohol. It dissolves in hot alcohol, and the soln. crystallizes on cooling. The same salt is formed by the spontaneous evaporation of a soln. of the component salts in the proportion $N_2H_4.2HCl : HgCl_2 = 2 : 1$. M. Adams reported **hydroxylamine trichlorodimercuriate,** $(NH_3OH)HgCl_3$, *i.e.* $HgCl_2.NH_2OH.HCl$; and **decahydroxylamine enneachlorodimercuriate,** $2HgCl_2.5(NH_2OH)_2HCl$, to be formed from soln. of the component salts. The latter is formed at a low temp., −10°.

W. Herz and W. Paul[5] found that at 25° soln. containing 0, 4·14, 17·38, and 35·27 milligram-mols of lithium chloride in 10 c.c. of water dissolved respectively 2·65, 3·51, 16·78, and 30·62 milligram-mols of mercuric chloride, and that the ratio for the more conc. soln. approximated to that required for $LiCl.HgCl_2$. In 1829, P. A. von Bonsdorff claimed to have prepared needle-like crystals of a deliquescent double salt of lithium and mercuric chlorides; and, in 1893, E. C. Linebarger inferred the existence of **lithium trichloromercuriate,** $LiHgCl_3$, *i.e.* $HgCl_2LiCl$, in aceto-acetic ether soln., because of the solubility of lithium chloride in soln. of mercuric chloride in this solvent:

	0°	10°	20°	30°	40°
Mols $HgCl_2$ per litre	8·2	0·9	6·3	0·6	6·4
Mols LiCl per litre	8·5	1·0	6·5	0·9	6·8

According to R. Varet, the heat of formation of this salt in soln. at 17° is 0·9 Cal. F. Calzolari and U. Tagliavini obtained lithium mercuric chloride, or lithium chloromercuriate, $LiCl.HgCl_2$, which could not be crystallized, but complexes with hexamethylenetetramine were readily formed. P. Harth made **lithium tetrachloromercuriate,** Li_2HgCl_4, *i.e.* $HgCl_2.2LiCl$, by adding mercuric chloride to a sat. soln. of lithium chloride so long as any is dissolved. Needle-like crystals of the salt in question are deposited when the soln. is evaporated in vacuo. The salt decomposes when dried in vacuo; it is very hygroscopic; very soluble in water; and, according to R. Varet, has a heat of formation, in soln. at 17°, of 0·8 Cal.

J. Davy[6] noted a soln. of sodium chloride dissolves a far greater proportion of mercuric chloride than is dissolved by water alone; and that rhomboidal

crystals of a double salt are obtained by cooling to 15° a warm soln. of 7 parts of sodium chloride and 35 parts of mercuric chloride in 20 parts of water. K. Voit obtained not the double salt $2NaCl.HgCl_2$, but crystals of mercuric chloride. W. Herz and W. Paul measured the solubility of mercuric chloride in soln. of different proportions of sodium chloride at 25°, and found soln. containing 0, 2·12, 11·53, 19·41, and 31·62 milligram-mols of sodium chloride in 10 c.c. of water dissolve respectively 2·65, 3·72, 11·92, and 34·34 milligram-mols of mercuric chloride; in the more conc. soln., the ratio $NaCl : HgCl_2$ approximates to that required for the formation of the salt $NaCl : HgCl_2$. J. Davy found that warm soln. take up much more of these salts and, on cooling, deposit the same. J. Müller showed that a soln. with at least 10 times as much sodium as potassium chloride does not give some of the reactions characteristic of mercuric chloride—for instance, it does not coagulate albumen. J. von Liebig prepared needle-like crystals of what were regarded as **sodium tetrachloromercuriate,** $2NaCl.HgCl_2$, or Na_2HgCl_4, by precipitation from mixed soln. of the component salts. K. Voit also reported the formation of crystals of the same salt, but there is some doubt about its existence. A. Benrath inferred the existence of the complex salt Na_2HgCl_4 in aq. soln. from the lowering of the f.p. and the raising of the b.p.; and M. le Blanc and A. A. Noyes also from the electrical conductivities of these soln.

In a soln. of two salts *A* and *B* with a common ion present in excess only one sat. soln. is possible provided the salts do not form a double salt with one another.[7] If the two salts do form a double salt *AB*, two sat. soln. will be possible, (1) when *A* and *AB* are present as solids, and (2) when *AB* and *B* are present. The single salts alone or a double salt alone can exist in contact with a series of sat. soln. containing *A* and *B*. Consequently, when *two* separate salts are present in the residue, the relative composition of the residue will change as the relative composition of the soln. changes, but the composition of the sat. soln. will remain constant; and when one salt—simple or double—is alone present in the residue, the composition of the residue will remain fixed, while the composition of the sat. soln. will vary. Consequently, if the composition of the residue varies in different determinations while that of the soln. remains constant, two salts are present in the system; while if the composition of the soln. varies while that of the residue remains constant, only one salt—single or double—is present in the system. In applying the method to practice, weighed quantities of the two salts *A* and *B* are placed in test-tubes containing a definite amount of solvent. The quantity of salts and solvent are so regulated that there is always an undissolved residue at the temp. of the experiment. The relative amounts of each salt are varied systematically in different test-tubes. The composition of the soln. can be determined by analysis, and that of the residue calculated provided the solids are anhydrous; when the salts contain water of crystallization the residue must also be analyzed.

The results obtained by H. W. Foote and L. H. Levy[8] for soln. of sodium and mercuric chlorides at 25°, when the solubility of the former is 36·50 per cent., are as follows:

Per cent. NaCl soln.	18·66	18·71	18·87	14·97	14·03	13·17	12·97	13·15
NaCl in residue .	83·64	78·02	28·75	16·38	16·36	15·96	11·80	9·17
Solid phase . .	$NaCl+NaHgCl_3.2H_2O$			$NaHgCl_3.2H_2O$			$NaHgCl_3.2H_2O+HgCl_2$	

The results are plotted in Fig. 16. The vertical lines—soln. variable, residue constant—represent soln. with the solid phase of constant composition in aq. soln. at 25°; the horizontal lines—soln. constant, residue variable—represent mixtures of salts. From this result it appears as if the only double salt formed at 25° is **dihydrated sodium trichloromercuriate,** $NaCl.HgCl_2.2H_2O$ or $NaHgCl_3.2H_2O$; and similar results were observed at 10·3°. Had the compound $2NaCl.HgCl_2$ or Na_2HgCl_4 been formed, the first three solubilities in the table would have been different. The similarity in the solubilities, and the variability in the composition of the

residues, show that a mixture of these two salts is involved. P. A. von Bonsdorff prepared sodium trichloromercuriate in 1829 by shaking a sat. soln. of sodium chloride with powdered mercuric chloride until the system was in equilibrium. Crystals of this double salt were obtained by C. Tourneux, by the spontaneous evaporation of the filtered soln. R. Schindler, and K. Voit likewise prepared needle-like crystals of this salt in an analogous manner. The earlier investigators supposed the salt to have the composition $NaHgCl_3.1\frac{1}{2}H_2O$. The salt melts at 100° in its own water of crystallization, part of which evaporates with the loss of a little mercuric chloride; when heated more strongly, the soln. boils, mercuric chloride and water are driven off, and sodium chloride remains. Water dissolves 75 per cent. of the salt at 15°, and it can be crystallized unchanged from the aq. soln. J. L. Lassaigne found that ether extracts the salt from its aq. soln. Alcohol dissolves the salt copiously. The general reactions of the salt resemble those of mercuric chloride. E. C. Linebarger found at 0°, a soln. of 4·4, 12·0, and 22·0 mols of mercuric chloride in acetone dissolved respectively 4·4, 11·2, and 22·9 mols of sodium chloride in agreement with the existence of $NaHgCl_3$ in these soln.; analogous results were obtained at 5° and 10°. H. W. Foote says that in alcoholic soln. of mercuric and sodium chlorides no double salt is formed in the absence of water. E. C. Linebarger found also that the double salt is not formed in benzene soln., but in acetone soln. $NaCl.HgCl_2$ is formed, and K. Voit says the anhydrous salt is made when the dihydrated salt is evaporated over sulphuric acid. According to R. Varet, the heat of formation from its constituents in soln. at 17° is ($HgCl_2$, NaCl) 0·85 Cal. E. C. Linebarger reported a salt $NaCl.HgCl_2.H_2O$, but this has not been confirmed; he said the salt decomposes when treated with ethyl acetate into sodium chloride and **sodium pentachloromercuriate,** $NaHg_2Cl_5$, or $NaCl.2HgCl_2$; and he accordingly prepared sodium pentachloromercuriate by the action of ethyl acetate on sodium trichloromercuriate; sodium chloride precipitates, and on evaporation of the soln., the salt in question is obtained. He also made it by mixing soln. of the component salts in ethyl acetate. The salt is said to form long needle-like crystals soluble in acetone and in ethyl acetate; it is not stable in benzene soln.; and it is only slightly dissociated in dil. soln. of acetoacetic ester between 0° and 50°. For example, E. C. Linebarger found that soln. of 2·5 (41·8°), 17·1 (48°), and 21·1 (30°) mols of mercuric chloride per litre of acetoacetic ester dissolved respectively 1·2 (41·8°), 8·4 (48°), and 10·7 (30°) mols of sodium chloride. The b.p. of the soln. of mercuric chloride in acetoacetic ether is not changed by adding sodium chloride. The salt, however, is decomposed at higher temp., and sodium chloride is precipitated. E. C. Linebarger could find no evidence of the formation of a double salt of mercuric and sodium chloride in benzene soln.

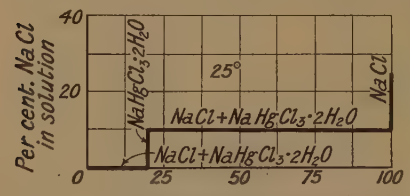

FIG. 16.—Solubility of Mixed Solutions of Sodium and Mercuric Chlorides.

In 1822, J. Davy[9] found a warm soln. of 7 parts of potassium chloride in 21 parts of water dissolved 8 parts of mercuric chloride, and when cooled to 15·5°, deposited a few needle-like crystals, and at 10°, it almost completely solidified to a mass of similar crystals. W. Herz and W. Paul found a soln. with 0, 2·21, and 6·83 milligram-mols of potassium chloride in 10 c.c. of water at 25°, dissolved respectively 2·65, 3·81, and 8·36 milligram-mols of mercuric chloride. A. Benrath measured the lowering of the f.p. and the raising of the b.p. of these soln., and considered that the results showed that a complex K_4HgCl_6 is present in these soln. M. le Blanc and A. A. Noyes found evidence of the formation of complexes in the electrical conductivities of mixed soln.; and O. Schönrock obtained similar evidence in the electromagnetic rotation of the plane of polarization—he found marked deviations in the results with mixed soln. of the component salts from the mixture rule.

P. A. von Bonsdorff described three double mercuric and potassium chlorides.

Writing the mol. ratio in the order $HgCl_2$: KCl, H_2O, P. A. von Bonsdorff's three salts were 1 : 2 : 1, 1 : 1 : 1, and 2 : 1 : 2. H. W. Foote obtained similar results as the stable phases in aq. soln. of different proportions of the two component salts at 25° ; but V. Tichomiroff studied the ternary system, $HgCl_2$—KCl—H_2O, at 20°, and obtained different results from H. W. Foote, for he found the anhydrous salts 1 : 2 : 0, 1 : 1 : 0, and 2 : 1 : 0. When mercuric chloride is continuously added to a sat. soln. of potassium chloride, the solubility of the latter is reduced and potassium chloride separates from the soln. After a time, the double salt $HgCl_2.2KCl$ commences to separate ; and no change in the solubility occurs until all the solid potassium chloride has been converted into this salt. Further additions of mercuric chloride again depress the solubility until the double salt $HgCl_2.KCl$ commences to separate. The phenomenon previously described is repeated with this salt ; and still again with the double salt $2HgCl_2.KCl$.

H. W. Foote gave for equilibrium in the system $HgCl_2$—KCl—H_2O, at 25° :

Per cent. KCl . .	26·46	23·74	21·39	17·85	6·66	6·27	5·77
Residue . . .	100·00	34·61	34·80	21·89	20·54	12·09	11·87
Solid phase . .		1 : 2 : 1		1 : 1 : 1		2 : 1 : 2	

V. Tichomiroff believed that with soln. containing from no mercuric chloride and 34·41 grms. of potassium chloride up to 19·33 grms. of mercuric chloride and 41·33 grms. of potassium chloride in 100 parts of water, the solid phase is KCl; between the latter conc. and up to 42·84 grms. of mercuric chloride and 34·12 grms. of potassium chloride, the solid phase is $HgCl_2.2KCl$; between the latter conc. and 26·41 grms. of mercuric chloride and 7·39 grms. of potassium chloride, the solid phase is $HgCl_2.KCl$; between the latter conc. and up to 26·41 grms. of mercuric chloride and 4·84 grms. of potassium chloride, the solid phase is $2HgCl_2.KCl$; and between the latter conc. and 7·39 grms. of mercuric chloride and no potassium chloride, the solid phase is $HgCl_2$. V. Tichomiroff's results are shown in Fig. 17, where the solid phases of the double salts are represented as a ratio $HgCl_2$: KCl, without showing the water of crystallization.

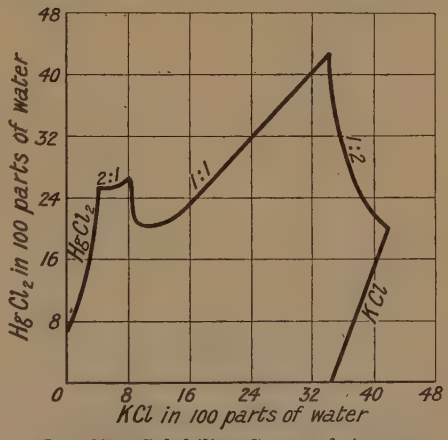

Fig. 17.—Solubility Curve of Aqueous Solutions of Mercuric and Potassium Chlorides, at 20°.

The results of C. Tourneux's study of the ternary system at 34°, 56°, 80°, and 100° are illustrated in Fig. 18. At 34°, the solid phases are KCl ; *AB*, Fig. 18 ; $HgCl_2.2KCl.H_2O$, *BC* ; $HgCl_2.KCl.\frac{3}{4}H_2O$, *CH* ; $3HgCl_2.2KCl.\frac{5}{3}H_2O$, *HI* ; $2HgCl_2.KCl.2H_2O$, *IJ*, and $HgCl_2$. At 50°, the phase $2HgCl_2.3KCl.\frac{5}{3}H_2O$ has appeared, and $2HgCl_2.KCl.2H_2O$ has disappeared. The zones of stability of the different solid phases between 34° and 100° are *ABED*, for KCl ; *BCFE*, for $HgCl_2.2KCl.H_2O$; *CFG*, for $2HgCl_2.3KCl.\frac{5}{3}H_2O$; *CHMG*, for $HgCl_2.KCl.\frac{3}{4}H_2O$; *HILM*, for $3HgCl_2.2KCl.\frac{5}{3}H_2O$; and *IJK*, for $2HgCl_2.KCl.2H_2O$. C. Tourneux is not certain whether or not the salt $3HgCl_2.2KCl.\frac{5}{3}H_2O$ is not a solid soln. of $(2HgCl_2.KCl.H_2O)_4(HgCl_2.2KCl.H_2O)$; $HgCl_2.KCl.\frac{3}{4}H_2O$, a solid soln. of $(2HgCl_2.KCl.H_2O)(HgCl_2.2KCl.H_2O)$; and $2HgCl_2.3KCl.\frac{5}{3}H_2O$, a solid soln. of $(2HgCl_2.KCl.H_2O)(HgCl_2.2KCl.H_2O)_4$. He believed the component salts of these assumed mixed crystals are homœomorphic. In acetone soln., at 25°, H. W. Foote obtained as solid phases $HgCl_2.KCl : C_3H_6O$, and the salts 5 : 1 : 1, and 6 : 5 : 2 ; and in ethyl alcohol soln., the solid phase $6HgCl_2.5KCl.2C_2H_5OH$.

The crystals indicated above, obtained by J. Davy, were **monohydrated potassium tetrachloromercuriate,** $K_2HgCl_4.H_2O$, or $HgCl_2.2KCl.H_2O$. J. von Liebig prepared it by precipitation with alcohol from a mixed aq. soln. of potassium chloride and an excess of mercuric chloride. P. A. von Bonsdorff evaporated a soln. of eq. quantities of the two salts; and C. F. Rammelsberg a soln. of one mol of mercuric chloride with four mols of potassium chloride. According to H. W. Foote, the salt when recrystallized from water gives the 1 : 1 : 1 salt; C. F. Rammelsberg, E. H. Kraus, and J. Grailich say that the crystals belong to the rhombic system and have axial ratios $a : b : c$ 0·7074 : 1 : 0·7655. C. Tourneux gave 3·58 for the sp. gr. at 15°/15°, 0·279 for the sp. vol., and 122 for the mol. vol. J. Thomsen said that the heat of soln. of a mol of mercuric chloride in a soln. of two mols of potassium chloride is —1·38 Cals.; (Hg, Cl_2, 2HCl, Aq.)=61·78 Cals.; ($HgCl_2$, 2KCl, H_2O)=6·13 Cals.; M. Berthelot gave ($HgCl_2$, 2KCl, H_2O)=5·40 Cals.; $HgCl_2.2KCl$)=3·80 Cals.; and for the heat of soln. of $HgCl_2.2KCl$, —15 Cals., and for $HgCl_2.2KCl$, H_2O, —16·6 Cals. J. Thomsen gives for the heat of soln. of $K_2HgCl_4.H_2O$ in $600H_2O$, —16·39 Cals.; and R. Varet, for the heat of formation in aq. soln., ($HgCl_2$, 2KCl), 0·80 Cal.

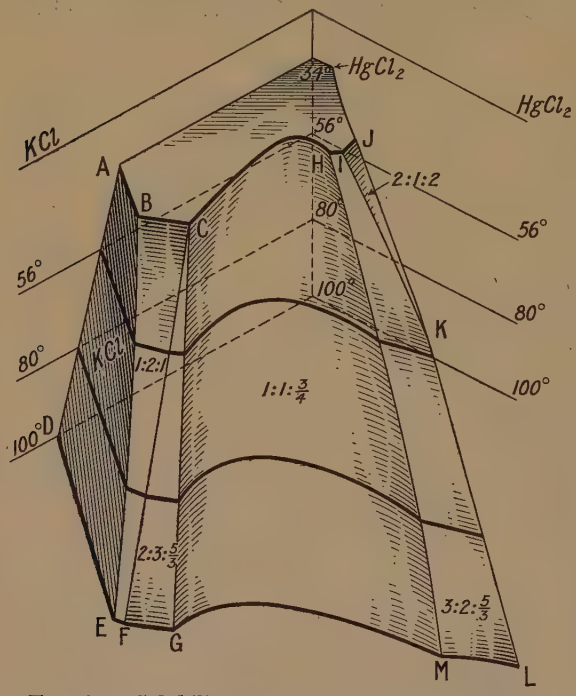

FIG. 18.—Solubility Curves of Aqueous Solutions of Mercuric and Potassium Chlorides between 34° and 100°.

E. C. Linebarger claimed to have made the anhydrous **potassium trichloromercuriate,** $KHgCl_3$, or $HgCl_2.KCl$, by adding gradually to a sat. soln. of mercuric chloride in acetoacetic ester an equi-molar proportion of potassium chloride. H. W. Foote made **monohydrated potassium trichloromercuriate,** $KHgCl_3.H_2O$, by shaking a soln. of the component salts; P. A. von Bonsdorff made it by digesting at 30°, a soln. of potassium chloride, sat. in the cold, with an excess of mercuric chloride. The evaporation of the clear filtrate first gives a crop of crystals of $2HgCl_2.KCl.2H_2O$, followed by a crop of crystals of $HgCl_2.KCl.H_2O$. P. F. G. Boullay made the same salt by neutralizing with potassium hydroxide a soln. of mercuric chloride in hydrochloric acid. C. Tourneux obtained this salt, but he suggested that it is a solid soln. of the 2 : 1 : 2, and the 1 : 2 : 1 salts. The crystals are acicular, and appear in the form of four-sided prisms, which H. W. Foote recrystallized from water unchanged. P. A. von Bonsdorff said that the crystals are easily soluble in water, and sparingly soluble in alcohol. M. Berthelot gives the heat of formation ($HgCl_2$, KCl), 2·4 Cals.; ($HgCl_2$, KCl, H_2O), 4·2 Cals.; and for the heat of soln. of the former, —9·5 Cals., and of the latter, —11·3 Cals.

P. A. von Bonsdorff made needle-like crystals of **dihydrated potassium pentachlorodimercuriate,** $2HgCl_2.KCl.2H_2O$, or $KHg_2Cl_5.2H_2O$, by shaking a soln. of potassium chloride, sat. at 50° to 60°, with powdered mercuric chloride, and then cooling the soln. C. F. Rammelsberg evaporated a mixed soln. of two mols of

potassium chloride with one mol of mercuric chloride. H. W. Foote made this salt by shaking the component salts with water at 25°. P. F. G. Boullay made it by neutralizing with potassium hydroxide, a sat. soln. of mercuric chloride in boiling hydrochloric acid. C. Tourneux could not make the monohydrate $2HgCl_2.KCl.H_2O$. According to H. W. Foote, the salt gives mercuric chloride when recrystallized from water. The rhombic crystals when heated in open vessels lose their contained mercuric chloride; they are very soluble in warm water, and sparingly soluble in alcohol. C. Tourneux gave 4·11 for the sp. gr. at 15°/15°, 0·243 for the sp. vol., and 159 for the mol. vol. M. Berthelot gave the heats of formation of some imaginary salts 3 : 4 : 0, 3 : 4 : 3, and 1 : 4 : 0.

R. Godeffroy prepared the double salts of mercuric and rubidium chlorides with $HgCl_2 : RbCl : H_2O$ in the ratio 1 : 2 : 0, 1 : 2 : 2, and 1 : 1 : 0, but H. W. Foote and L. H. Levy were unable to obtain any of these, for they found that at 25°, the solid phases in aq. soln. are the 5 : 1 : 0, 4 : 3 : 1, 1 : 1 : 1, 2 : 3 : 2, and the 1 : 2 : 1 salts, although H. W. Foote and L. H. Levy's salt 1 : 2 : 1 lies between R. Godeffroy's 1 : 2 : 0 and 1 : 2 : 2. According to H. W. Foote and L. H. Levy, the percentage solubilities of rubidium and mercuric chlorides are respectively 48·57 and 6·90 at 25°; and the ranges of stabilities of the solid phases for different percentage compositions of the soln. are :

RbCl . .	47·65	35·16	30·27	29·20	23·81	10·87	10·06	5·10	2·98	1·10
$HgCl_2$ . .	10·35	19·58	20·17	20·55	18·71	10·42	9·86	8·33	7·71	7·21
Solid phases .	1 : 2 : 1		2 : 3 : 2		1 : 1 : 1		4 : 3 : 1		5 : 1 : 0	

H. W. Foote and L. H. Levy's curve, shown in Fig. 19, indicates the range of stability for **rubidium henadecachloropentamercuriate,** $5HgCl_2.RbCl$, or

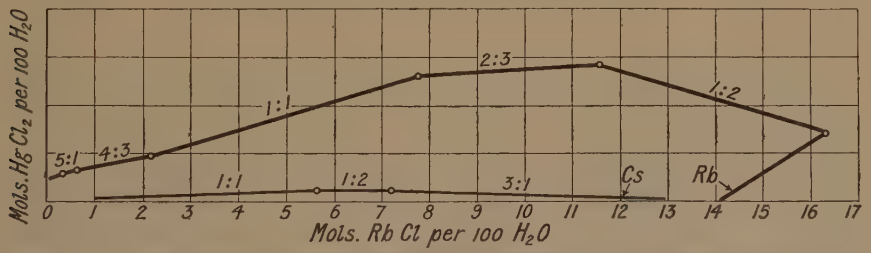

Fig. 19.—Compositions of Aqueous Solutions of Cæsium or Rubidium and Mercuric Chlorides in Equilibrium with the Solid Phases (25°).

$RbHg_5Cl_{11}$; when this salt is recrystallized from water, it gives crystals of mercuric chloride. R. Godeffroy claimed to have prepared silky needle-like crystals of **rubidium pentachlorodimercuriate,** $2HgCl_2.RbCl$, or $RbHg_2Cl_5$, by evaporating a soln. with equal parts by weight of the component salts, but H. W. Foote and L. H. Levy did not find this salt amongst the solid phases in equilibrium with aq. soln at 25°; rather did they obtain silky crystals of **monohydrated rubidium henadecachloro-tetramercuriate,** $4HgCl_2.3RbCl.H_2O$, or $Rb_3Hg_4Cl_{11}.H_2O$, from soln. with the composition indicated in the above table. C. Tourneux also made this salt. It gives the 5 : 1 salt when recrystallized from water. R. Godeffroy made **rubidium trichloromercuriate,** $HgCl_2.RbCl$, or $RbHgCl_3$, by heating $RbCl.2HgCl_2$ to 150° when mercuric chloride is volatilized and $RbHgCl_3$ remains. H. W. Foote and L. H. Levy made the monohydrated salt from soln. with the composition indicated in the preceding table. C. Tourneux also made this salt. When recrystallized from water, this salt furnishes the 4 : 3 : 1 salt. The same investigators obtained **dihydrated rubidium heptachloro-dimercuriate,** $2HgCl_2.3RbCl.2H_2O$, or $Rb_3Hg_2Cl_7$, from soln. with the composition indicated in the preceding table; and it yields the 4 : 3 : 1 salt when recrystallized from water. R. Godeffroy reported that needle-like crystals of **tetrahydrated rubidium tetrachloromercuriate,** $HgCl_2.2RbCl$, or

Rb_2HgCl_4, separated by evaporating the hydrochloric acid soln. of the constituents, and he also reported colourless prisms of the dihydrated salt to be formed by the evaporation of an aq. soln. of the anhydrous salt; but H. W. Foote and L. H. Levy could get only the monohydrated salt from soln. whose composition is indicated in the preceding table. When recrystallized from water it gives the 4 : 3 : 1 salt.

R. Godeffroy reported the double salt $HgCl_2.2CsCl$ in 1875; and H. L. Wells prepared five double salts of mercuric and cæsium chlorides with $HgCl_2$: CsCl, all of which—5 : 1, 2 : 1, 1 : 1, 1 : 2, and 1 : 3—were anhydrous in aq. soln. at 25°. It might have been expected that cæsium, the extreme member of the potassium groups, and the most electropositive of the metals, would form a more complete series of double salts than the other alkali metals, and this the more because the cæsium double salts are usually less soluble than the corresponding salts of the other alkali metals. It will also be observed that the variety of the cæsium double salts is greater with mercury than with cadmium, since mercury gives six types of halide double salts, while cadmium gives but three. Zinc also gives but two and magnesium one. Hence, the variety of double salts with these bivalent elements increases with the at. wt. of the element. Representing the ratios $HgCl_2$: MCl : H_2O in the double salts of mercuric and the alkali chlorides, the following scheme indicates those salts whose existence as chemical individuals is fairly well established :

NaCl	NH_4Cl	KCl	RbCl	CsCl
..	..	..	5 : 1 : 0	5 : 1 : 0
..	9 : 2 : 0	..	..	..
..	..	2 : 1 : 1	..	2 : 1 : 0
..	3 : 2 : 1	..	..	..
..	..	..	4 : 3 : 1	..
1 : 1 : 1	1 : 1 : 1	1 : 1 : 1	1 : 1 : 1	1 : 1 : 0
..	..	..	1 : 3 : 2	..
..	1 : 2 : 1	1 : 2 : 1	1 : 2 : 1	1 : 2 : 0
..	..	..	..	1 : 3 : 0

C. Tourneux added that the double salts are all homœomorphic, and show marked chemical analogies. The dehydration curves show analogies with those of the zeolites, and suggest that the water content of the crystals depends on the vap. press. of the surrounding atm.

H. W. Foote applied the phase rule solubility method to aq. soln. of cæsium and mercuric chlorides, and the solid phases were found to be the same as those described by H. L. Wells. According to H. W. Foote, the percentage solubilities of cæsium and mercuric chlorides are 65·61 and 6·90, respectively, at 25°; and the ranges of stability of the solid phases for soln. of different percentage composition are :

CsCl	62·36	52·35	49·30	45·95	38·63	1·53	0·49	0·40	0·41	0·25
$HgCl_2$	0·32	1·23	1·49	1·69	1·32	0·42	2·91	3·78	4·68	5·65
Solid phases	1 : 3		1 : 2		1 : 1		2 : 1		5 : 1	

A portion of the curve for the ranges of stability is shown in Fig. 18. The experimental results with mixtures of cæsium and mercuric chlorides are illustrated by the graph, Fig. 20. The vertical lines—soln. variable, residue constant—correspond with the five double salts $CsCl : HgCl_2$ as 3 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 5, which are therefore stable in aq. soln. at 25°. The horizontal lines—soln. constant, residue variable—indicate mixtures of salts represented by the adjacent vertical lines. There was an irregularity observed in the numbers relating to the 1 : 1 salt, $CsCl.HgCl_2$ or $CsHgCl_3$, for the experiments showed at first a slight decrease and then a slight increase in the proportion of mercuric chloride along the $CsHgCl_3$ line. This corresponding with a change in the nature of the double salt in spite of a change in composition. This change is presumably connected with the known dimorphism—cubic and rhombic—of this salt; there is only one definite transition temp. at which both forms are stable, and it might therefore be expected that one form alone would

appear at the arbitrary temp. 25°. However, the conditions are not the same in different experiments. When the cæsium salt largely predominates, the cubic form is stable; if otherwise, the rhombic form is stable. According to the phase rule, when the double salt is present there are four phases in the system—two solids, soln., vapour—and three components. The system is therefore univariant. If the temp. be variable, the conc. of the soln. will remain constant, and if one phase disappears, the soln. becomes bivariant, when both temp. and conc. may be varied.

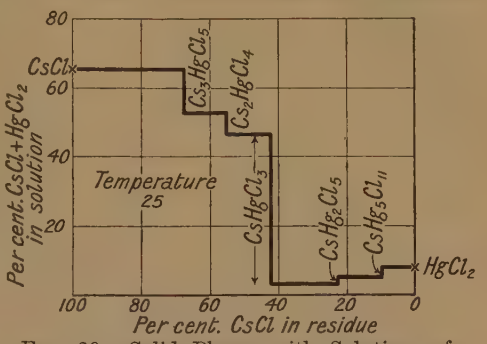

FIG. 20.—Solid Phases with Solutions of Mercuric and Cæsium Chlorides.

H. L. Wells made **cæsium henadecachloropentamercuriate,** $5HgCl_2.CsCl$, or $CsHg_5Cl_{11}$, by cooling a boiling aq. soln. of a mol of cæsium chloride with six mols of mercuric chloride. D. Strömholm prepared it by the action of a soln. of mercuric and cæsium chlorides in ethylsulphine chloride, $(C_2H_5)_3SCl$. According to S. L. Penfield, the prismatic crystals are monoclinic with the axial ratios $a:b:c=0{\cdot}7233:1:0{\cdot}4675$, and $\beta=85°\ 51'\ 40''$. According to H. W. Foote and L. H. Levy, when recrystallized from water it furnishes the 2 : 1 salt. H. L. Wells also made **cæsium pentachlorodimercuriate,** $2HgCl_2.CsCl$, or $CsHg_2Cl_5$, by cooling a soln. of 24 grms. of $CsHgCl_2$ and 16 grms. of mercuric chloride in hot water. According to H. W. Foote and L. H. Levy, when recrystallized from water it furnishes the 1 : 1 salt. According to S. L. Penfield, the monoclinic prismatic crystals have the axial ratios $a:b:c=1{\cdot}6099:1:1{\cdot}3289$, and $\beta=101°\ 6'$. As indicated above, **cæsium trichloromercuriate** is dimorphous. Cubic crystals of the salt are formed by cooling mixed soln. with a large excess of cæsium chloride or by crystallizing the salt from a soln. of alcohol (1 : 3). It is almost insoluble in absolute alcohol. The rhombic crystals are deposited when the cæsium chloride is not in excess, and by one or more crystallizations from water of any of the double cæsium chlorides. According to S. L. Penfield, the axial ratios are $a:b:c=0{\cdot}5774:1:0{\cdot}4088$; and the refractive index $\mu=1{\cdot}779$ for the lithium ray, and 1·792 for the sodium ray. The salt can be recrystallized from water unchanged, and at 17°, the aq. soln. contains 1·406 per cent. of this salt. R. Godeffroy made **cæsium tetrachloromercuriate,** $HgCl_2.2CsCl$, or Cs_2HgCl_4, by mixing soln. of the constituents in hydrochloric acid, and H. L. Wells by crystallization from a hot soln. of mercuric chloride in a nearly sat. soln. of cæsium chloride. The crystal constants have not been measured. The salt is very soluble in water. When recrystallized from water, crystals of the 1 : 1 salt are formed. H. L. Wells also made pyramidal prismatic crystals of **cæsium pentachloromercuriate,** $HgCl_2.3CsCl$, or Cs_3HgCl_5, by dissolving a comparatively small quantity of mercuric chloride in a rather less quantity of a nearly sat. soln. of cæsium chloride than is required for the preceding salt. H. W. Foote's work on the mutual solubility of mercuric and cæsium chlorides shows the conditions of stability. S. L. Penfield found the crystals belong to the rhombic system and have the axial ratios $a:b:c=0{\cdot}7976:1:0{\cdot}6605$. When crystallized from water it gives the 1 : 1 salt.

P. A. von Bonsdorff [10] reported the formation of a double salt, *cupric tetrachloromercuriate,* $HgCl_2.CuCl_2$, by mixing aq. soln. of the component salts, and T. Harth also claimed to have made it in greenish-blue needle-like crystals by evaporating a soln. sat. with both components. The crystals are easily soluble in water, they are probably mixed crystals because, in spite of R. Varet's values for the heats of formation in soln.—($CuCl_2$, $HgCl_2$), 1·2 Cals. at 18°, and ($CuCl_2$, $2HgCl_2$), 1·36 Cals. at 17°—F. A. H. Schreinemakers and J. C. Thonus could find no evidence of the

formation of a double salt in aq. soln. at 35° when examined by the solubility method. The isothermal line *ac* in Fig. 21 represents soln. sat. with $CuCl_2.2H_2O$; and *bc*, soln. sat. with $HgCl_2$. The point of intersection *c* represents soln. sat. with both these salts. The solubility of mercuric chloride, *bc*, Fig. 21, is greatly increased by the addition of cupric chloride rising from 8·5 per cent. in water alone to 52·8 per cent. when 18·06 per cent. of cupric chloride is present. P. A. von Bonsdorff also claimed to have made rhombic crystals of the ternary salt, $3HgCl_2.CuCl_2.6KCl.2H_2O$, by crystallization from mixed soln. of $HgCl_2.KCl.H_2O$ and $CuCl_2.KCl.H_2O$. A. Mailhe also reported two *cupric mercuric oxychlorides*, $3CuO.HgCl_2.H_2O$ and $7CuO.CuCl_2.HgCl_2.2H_2O$, which are probably mixtures.

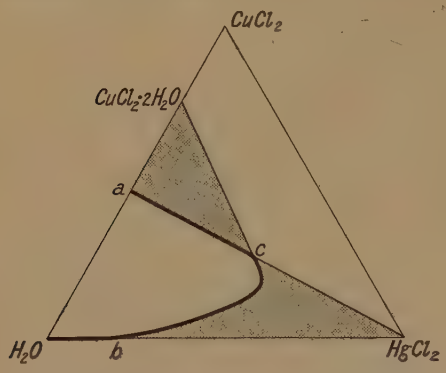

FIG. 21.—Solubility curves in the Ternary System, $CuCl_2$—$HgCl_2$—H_2O at 35°.

The chloromercuriates of the alkaline earths have not been so closely investigated as those of the alkali metals. W. Herz and W. Paul have studied the solubilities of mercuric chloride in soln. of the chlorides of the alkaline earths; T. W. Richards and E. H. Archibald found that when calomel is shaken with soln. of barium or calcium chloride, the dissolved mercury exists wholly in the mercuric state. As the conc. of the calcium or barium chloride is increased, the quantity of mercuric chloride in soln. increases as a simple function of the square of the conc. of the chlorine ions. The results are explained by assuming that a highly ionized complex $CaHgCl_4$ or $BaHgCl_4$ is produced. P. A. von Bonsdorff reported octahedral crystals of **octohydrated calcium dodecachloropentamercuriate,** $CaCl_2.5HgCl_2.8H_2O$, or $CaHg_5Cl_{12}.8H_2O$, to be formed by the slow evaporation of a soln. of calcium chloride not completely sat. with mercuric chloride. D. Strömholm also made analogous crystals by a similar process which his analyses represented as $CaCl_2.6HgCl_2.6H_2O$. P. A. von Bonsdorff made rhombic plates of **hexahydrated calcium hexachloromercuriate,** $CaCl_2.2HgCl_2.6H_2O$, by crystallization from a soln. of calcium chloride sat. with mercuric chloride. R. Varet gave the heat of formation in soln. at 17° as 0·98 Cal. P. A. von Bonsdorff prepared needle-like crystals of what he regarded as **strontium hexachlorodimercuriate,** $SrCl_2.2HgCl_2.2H_2O$, by the evaporation of sat. soln. of the component salts. J. N. Swan believed that P. A. von Bonsdorff's salt just described is really $SrCl_2.3HgCl_2.5(\text{or } 6)H_2O$. R. Varet computed the heat of formation in soln. at 17° to be 0·98 Cal. T. Harth's salts with the ratio $HgCl_2 : SrCl_2$ as 8 : 1, 8 : 5, 3 : 2, and 4 : 3 are probably mixtures.

J. Davy, in 1822, prepared crystals of what has been regarded as a double salt of barium and mercuric chlorides by dissolving 20 parts of mercuric chloride in a hot soln. of 8·7 parts of dihydrated barium chloride in 20 parts of water. P. A. von Bonsdorff obtained oblique rhombic prisms in a somewhat similar way, and his analyses correspond with $BaCl_2.2HgCl_2.2H_2O$, but J. N. Swan believed these crystals have rather the composition $BaCl_2.3HgCl_2.8H_2O$. H. W. Foote and H. S. Bristol, however, by an application of the solubility method, said that in aq. soln., at 25°, there is evidence of the formation of **hexahydrated barium octochlorotrimercuriate,** $BaCl_2.3HgCl_2.6H_2O$, or $BaHg_2Cl_8.6H_2O$, but not of P. A. von Bonsdorff's salt. This also agrees with F. A. H. Schreinemakers' observations. R. Varet has calculated the heat of formation of some possible barium chloromercuriates. C. Sandonnini observed no double compounds of strontium or barium chloride on the f.p. curves.

P. A. von Bonsdorff obtained rhombic crystals of **beryllium chloromercuriate** by the evaporation of an aq. soln. of the component salts, but he gave no analyses. A. Atterberg likewise obtained tabular hygroscopic crystals by evaporating a soln.

of equi-equivalents of the two chlorides in an excess of hydrochloric acid, but J. C. G. de Marignac claims that no double salt is formed since he obtained crystals of mercuric chloride alone. J. Davy obtained a crop of needle-like crystals by dissolving mercuric chloride in a warm soln. of magnesium chloride of sp. gr. 1·58; J. N. Swan found the crystals have the composition $MgCl_2.3HgCl_2.6H_2O$; and P. A. von Bonsdorff likewise obtained crystals of **magnesium octochlorotrimercuriate,** $MgCl_2.3HgCl_2.5(\text{or } 6)H_2O$, by evaporating a soln. of magnesium chloride sat. with mercuric chloride, and from the mother liquid he obtained rhombic prisms of **magnesium tetrachloromercuriate,** $MgCl_2.HgCl_2.6H_2O$. W. Herz and W. Paul have studied the solubility of mercuric chloride in soln. of magnesium chloride. F. Calzolari and U. Tagliavini obtained crystals of a complex of $MgCl_2.2HgCl_2.10H_2O$ with hexamethylenetetramine. R. Varet has computed the heats of formation of some possible double salts of magnesium and mercuric chlorides. According to P. A. von Bonsdorff, a soln. of mercuric chloride in an aq. soln. of zinc chloride on evaporation first deposits crystals of mercuric chloride, then deliquescent needles and plates of **zinc chloromercuriate** slowly separate out. C. Sandonnini found molten zinc and mercuric chlorides are incompletely miscible; two layers are formed each containing traces of the other constituent. K. Drucker measured the conductivity, distribution numbers, and the depression of the f.p. of aq. soln. of zinc and mercuric chlorides, and concluded that soln. with over 0·05 mol of these salts per litre contain a mixed complex which in the non-ionized condition contains four chlorine atoms, and is, in consequence, probably $ZnHgCl_4$, a compound which T. Harth claims to have prepared, but he gives no analyses. R. Varet has calculated the heats of formation of some possible zinc chloromercuriates; for $(ZnCl_2, HgCl_2)$ in aq. soln. at 17°, he gives 1·14 Cals. G. André has reported two **zinc ammino-chloromercuriates,** namely, $2ZnCl_2.HgCl_2.6NH_3.\frac{1}{2}H_2O$, and $4ZnCl_2.HgCl_2.10NH_3.3H_2O$. A. Mailhe has reported the oxychloride $CdO.HgCl_2.H_2O$; and R. Varet has calculated the heats of formation of some possible *cadmium chloromercuriates.*

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§ 16. Ammoniobasic and Aquo-ammonio-basic Salts of Mercuric Chloride

In the thirteenth century, Raymond Lully [1] obtained a *fusible white precipitate—perfectum præcipitatum*—by treating mercuric nitrate with sal ammoniac and salt of tartar ; this precipitate was later confused with calomel prepared by the wet process, and also with an infusible white precipitate obtained by N. Lemery by the action of ammonia on a soln. of mercuric chloride. Although J. Kunckel called both precipitated calomel and the fusible white precipitate *lac mercurii*, he said they are very different *in examine chymico ;* and F. Wöhler and R. J. Kane (1837) made clear the difference between all three preparations.

A great many different opinions have been promulgated as to the constitution or composition of infusible white precipitate, and in accord therewith it has been called by many different names. C. F. Rammelsberg and L. Pesci regarded it as a compound of ammonium chloride, NH_4Cl, with *mercuriammonium chloride*, NHg_2Cl, which was formed. H. Gaudechon [2] tried to show that it is a complex analogous with

$$Cl—N<\begin{matrix}Hg—Cl\\Hg—NH_4\end{matrix}$$

The general opinion now is that this compound is **mercuric chloroamide,** $Hg(NH_2)Cl$, or amido-mercuric chloride, $NH_2.Hg.Cl$; and is formed by the amminolysis of

mercuric diammino-chloride, $HgCl_2.2NH_3$, by a process analogous to the hydrolysis of salts. The amminolytic decomposition is symbolized: $HgCl_2.2NH_3 \rightleftharpoons NH_4Cl + NH_2.Hg.Cl$, and this emphasizes how the amminolysis is reversed by the accumulation of ammonium chloride in the system. While many amido-compounds are hydrolytically decomposed in the presence of water—*e.g.* potassamide—and can be formed from liquid ammonia or in the presence of solvents other than water, the compounds formed by the action of ammonia on mercuric salts can usually exist in the presence of water without appreciable hydrolysis.

In 1792, A. F. de Fourcroy described the preparation of mercuric chloroamide by the action of ammonia on mercuric chloride, and stated this substance is decomposed by heat into nitrogen, ammonia, and mercurous chloride. A similar method was used by H. Hennell and R. Brandes in 1825, and by R. J. Kane in 1836. An aq. soln. of mercuric chloride is treated with a slight excess of ammonia. The precipitate is washed with a small quantity of cold water, pressed between paper, and dried at a gentle heat. If the precipitate be washed with too much water, particularly with hot water, it acquires a yellow colour, owing to the formation of the chloride of the so-called Millon's base: HO.Hg.NH.Hg.Cl; the hydrolytic reaction is represented: $2NH_2.Hg.Cl + H_2O = NH_4Cl + HO.Hg.NH.Hg.Cl$. H. Hennell said that if 272 parts of mercuric chloride be precipitated by aq. ammonia containing 34 parts of ammonia, the filtrate is a soln. of neutral ammonium chloride; and G. Krug, that if the precipitation be made in the cold, and the precipitate rapidly separated from the mother liquid, a fairly pure product is obtained. R. J. Kane found that 270·8 parts of mercuric chloride furnish 252·2 parts and P. Geiseler 254·6 parts of infusible white precipitate. C. Tanret says that a white precipitate of this salt is formed when a 1 : 1000 soln. of mercuric chloride stands in air containing ammonia. H. Saha and K. N. Choudhuri dissolved freshly precipitated mercuric chloroamide in aqua ammonia, and evaporated the soln. over sulphuric acid in vacuo. The aggregates of small prismatic crystals were then washed with a little water, dried first in a desiccator, and finally at 100°.

Many other modifications of R. J. Kane's process have been described by G. André, E. Balestra, J. Sen, D. Strömholm, E. C. Franklin, etc. N. A. E. Millon, for example, dropped the mercuric chloride soln. into an excess of ammonia and, according to G. André, if N. A. E. Millon's procedure be followed with cold soln. of 33·875 grms. of mercuric chloride, and 4·25 grms. of ammonia per litre, and the precipitate be rapidly washed with cold water, a purer product is obtained than if R. J. Kane's process be used; he added that if an appreciable amount of hydrolysis has taken place, the precipitate, dried at 110°, will evolve water if heated to a higher temp.

E. C. Franklin obtained mercuric chloroamide by treating mercuric chloride with an excess of liquid ammonia, pouring off the excess of ammonia, and then washing the residue. There is a reaction: $HgCl_2 + 2NH_3 \rightleftharpoons Hg(NH_2)Cl + NH_4Cl$. In the liquid ammonia, the presence of a small quantity of ammonium chloride hinders the formation of the mercuric chloroamide, but in aq. soln., a large excess of ammonium chloride is needed to hinder its formation. D. Strömholm prepared mercuric chloroamide by agitating a mixture of mercuric diammino-chloride with aq. ammonia for five days until the conc. of the ammonium chloride remained constant. A. Duflos likewise obtained infusible white precipitate by adding ammonium carbonate to a soln. of mercuric chloride; *au contraire*, added G. S. Johnson, ammonium carbonate is far more potent than ammonium chloride in preventing the precipitation, for, even after complete precipitation, the addition of an excess of ammonium carbonate causes the precipitate to dissolve; he said that even the little carbon dioxide absorbed when it has stood in a loosely stoppered bottle, makes it unfit for the preparation of infusible white precipitate. D. J. Carnegie and F. Burt prepared it by treating a soln. of mercuric chloride with ammonium oxalate and sodium or ammonium phosphate. F. L. Winckler converted mercuric oxychloride into the chloroamide by agitating it with conc. aqua ammonia; and R. Varet

similarly converted mercuric chlorocyanide; E. C. Franklin agitated for some days the soln. of mercuric chloride in liquid ammonia with sodium amide, and the resulting product was washed to remove the sodium chloride and the excess of mercuric ammino-chloride. C. Barfoed found that the black product obtained by the action of ammonia on mercurous chloride when exposed to air in thin layers gradually loses mercury and becomes white or almost white mercuric chloroamide; and H. Saha and K. N. Choudhuri showed that the last-named salt can be dissolved from the black product by digesting it with conc. aqua ammonia.

As A. F. de Fourcroy [3] stated, mercuric chloroamide is a white powder which at first has an earthy taste and which afterwards appears to have the so-called metallic taste. H. Saha and K. N. Choudhuri obtained this salt in aggregates of small prismatic crystals. H. Gaudechon says the heat of formation of the reaction is: $NHg_2Cl+NH_4Cl=2Hg(NH_2)Cl+6{\cdot}8$ Cals. P. C. Ray and N. R. Dhar measured the electrical conductivity of aq. soln., and from the results inferred that the salt is decomposed into simpler parts, namely, NHg_2Cl and NH_4Cl. R. J. Kane showed that while mercuric chloroamide does not dissolve in *water*, it is slowly decomposed into a yellow product by cold water, and very quickly by boiling water; he found 502·8 parts of the white precipitate yield 450·3 parts of the yellow powder when treated with boiling water, and the water has taken up 51·5 parts of ammonium chloride. G. André has studied the progressive action of water on mercuric chloroamide, and has shown that the precipitate is gradually hydrolyzed, and D. Strömholm and H. Gaudechon have shown that with water there is a reversible reaction involving the formation of the chloride of Millon's base: $2Hg(NH_2)Cl+H_2O\rightleftharpoons NH_4Cl+HO.Hg.NH.Hg.Cl$, followed by the hydrolysis of the chloride of Millon's base: $HO.Hg.NH.Hg.Cl+H_2O\rightleftharpoons 2HgO+NH_4Cl$. The hydrolysis progresses more quickly if the water be hot, and in boiling water the reaction $2Hg(NH_2)Cl+H_2O=NH_4Cl+HO.Hg.NH.Hg.Cl$ is virtually completed in a few minutes.

When mercuric chloroamide is heated, very gently to about 340°, E. Mitscherlich found that some ammonia is first evolved without a trace of nitrogen, then follows the sublimation of mercuric chloride, and a red substance, $NHg_2Cl.HgCl_2$, remains. Consequently, the reaction is symbolized: $3Hg(NH_2)Cl=2NH_3+HgCl_2NHg_2Cl$, when heated below redness. R. J. Kane found mercuric chloroamide to be resolved without fusion into about 93 per cent. of mercurous chloride, and a mixture of one volume of nitrogen and two volumes of ammonia. This result has been confirmed by J. Sen, who found that two-thirds of the contained nitrogen is converted into ammonia, and one-third into nitrogen:

$$\begin{matrix} N & H_2 \\ NH_2 \\ NH_2 \end{matrix}\begin{matrix} HgCl \\ HgCl \\ HgCl \end{matrix} \rightarrow 2NH_3+3HgCl+\tfrac{1}{2}N_2$$

There are secondary reactions, for the mercurous chloride is usually blackened by the ammonia and some ammonium chloride is formed: $2NH_3+2HgCl=NH_4Cl+Hg+NH_2HgCl$.

According to H. Saha and K. N. Choudhuri, cold aq. *hydrofluoric acid* gives a mixture of ammonium fluoride and a fluorochloride, HgFCl. V. Schwarzenbach found that when mercuric chloroamide is exposed to the action of gaseous *chlorine* or chlorine water, all the contained nitrogen is evolved as a gas, and the mercury forms mercuric chloride; if the powder be projected into a globe filled with chlorine gas, it becomes hot and either explodes or produces a green flame—presumably owing to the formation of some nitrogen chloride. According to C. Ullgren, dry *hydrogen chloride* at 100° transformed the salt into a mixture of ammonium and mercuric chlorides—no water or mercuric oxide is formed—$Hg(NH_2)Cl+2HCl=HgCl_2+NH_4Cl$. A. F. de Fourcroy found it to be soluble in *hydrochloric acid*, forming a soln. of mercuric and ammonium chlorides, as was further established by H. Saha and K. N. Choudhuri. C. F. Rammelsberg found that a boiling conc.

soln. of *alkali chloride* separates ammonia from this compound, and mercuric chloride passes into soln., and G. André separated the nitrogen quantitatively as ammonia by this reaction. According to R. H. Brett, it is soluble in a hot soln. of *ammonium chloride*, and E. C. Franklin found that it is in equilibrium with a 0·49*N*-soln. of ammonium chloride: $HgCl_2.2NH_3 \rightleftharpoons Hg(NH_2)Cl+NH_4Cl$; and for the reversible reaction, $2Hg(NH_2)Cl+H_2O \rightleftharpoons HO.Hg.NH.Hg.Cl+NH_4Cl$, the conc. of the ammonium chloride is less. R. J. Kane found mercuric chloroamide to be decomposed when boiled with *cupric chloride;* a precipitate of the so-called Brunswick green, $CuCl_2.3CuO$, and a soln. of alembroth salt is formed. V. Schwarzenbach found that *bromine* acts like chlorine without forming nitrogen bromide; according to H. Edhem-Bey, a dil. alcoholic soln. of bromine acts vigorously on mercuric chloroamide, forming carbon tetrachloride, and a double salt, $NH_4Cl.HgBr_2$. Cold *hydrobromic acid*, said H. Saha and K. N. Choudhuri, gives a mixture of mercuric and ammonium bromides. According to K. A. Hofmann and E. C. Marburg, with a soln. of *ammonium bromide* ammonia is evolved. F. A. Flückiger noted that *hypobromous acid* or the alkali hypobromites decompose mercuric chloroamide in the presence of water, but less violently than iodine. H. Saha and K. N. Choudhuri say cold *hydriodic acid* gives a mixture of mercuric and ammonium iodides. According to V. Schwarzenbach, a mixture of finely divided mercuric chloroamide and an ethyl alcohol soln. of *iodine* first forms mercuric iodide, and then explodes with great violence; but dry iodine does not explode when rubbed up with mercuric chloroamide, or when the mixture is subjected to percussion, but F. A. Flückiger did obtain a detonation from a mixture of three parts of mercuric chloroamide and four parts of iodine which had been vigorously triturated and allowed to stand some time—iodine and nitrogen were developed. If two parts of iodine, in soln. in carbon disulphide, chloroform, glycerol, amyl or propyl alcohol in place of ethyl alcohol, be mixed with five of mercuric chloroamide, V. Schwarzenbach obtained no explosion in 24 hrs., but with six of iodine he did get an explosion owing to the formation of some nitrogen iodide. A mixture of water, iodine, and mercuric chloroamide decrepitated; F. A. Flückiger represented the reaction: $9Hg(NH_2)Cl+6I_2 = 3HgCl_2+6HgI_2+3NH_4Cl+2NH_3+2N_2$, and he adds that some nitrogen iodide, NHI_2, is formed as an intermediate product; according to C. Rice, the formation of explosive nitrogen iodide is prevented if some phenol be present, and iodoform, CHI_3, is then formed. R. J. Kane said that with an aq. soln. of *potassium iodide*, ammonia and mercuric iodide are formed. According to E. Rupp and F. Lehmann, the reaction is: $Hg(NH_2)Cl+2KI+H_2O=HgI_2+KCl+NH_3+KOH$.

According to V. Schwarzenbach, if mercuric chloroamide be heated to 150° with one-eighth of its weight of sulphur, the mixture becomes brown and a purple-red vapour of nitrogen sulphide, N_4S_4, is evolved; with equal weights of the two, the mixture becomes yellow at 150°, and a purple-red vapour of E. Soubeiran's *chloride de soufre ammoniacal*, $SCl_2.2NH_3$, is formed. R. J. Kane found that when mercuric chloroamide is heated with an aq. soln. of *barium sulphide*, ammonia and mercuric sulphide are formed. A. F. de Fourcroy noted that mercuric chloroamide is soluble in *sulphuric acid*, forming mercuric chloride, and mercuric and ammonium sulphates; according to C. Kosmann, if mercuric chloroamide be boiled with water acidified with sulphuric acid, and the soln. evaporated on a water-bath, white plate-like crystals of the triple salt, $2NH_4Cl.2HgSO_4.HgCl_2$, are formed, mercuric and ammonium sulphates remain in soln. According to G. André, dil. sulphuric acid does not decompose the salt even at 225° in a sealed tube. R. J. Kane could detect no reaction between *ammonia* and mercuric chloroamide, while D. J. Carnegie and F. Burt found mercuric chloroamide to be insoluble in an excess of ammonia; but H. Saha and K. N. Choudhuri found that if freshly precipitated the chloroamide dissolves in conc. aqua ammonia, and can be recovered in a crystalline form by evaporation. A. F. de Fourcroy and C. Kosmann found the salt to be soluble in dil. *nitric acid*, forming mercuric nitrate and ammonia; and R. H. Brett, soluble in a warm aq. soln. of *ammonium nitrate*, and, according to K. A. Hofmann and

E. C. Marburg, ammonia is slowly evolved. According to K. A. Hofmann and E. C. Marburg, with a neutral soln. of *silver nitrate* it gives up only half the contained chlorine during a 30 mins.' digestion; L. Pesci says the whole of the chlorine is given up by this treatment. B. E. Howard found that *hypophosphorous acid* reduces mercuric chloroamide to the metal when the mixture is warmed on a water-bath. D. J. Carnegie and F. Burt found that the salt is soluble in a conc. soln. of *phosphoric acid*, and the soln. deposits crystals of a compound not yet identified; it is also soluble in an excess of a soln. of *diammonium hydrogen phosphate*, but not in a soln. of *disodium hydrogen phosphate*. According to C. Reichard, a soln. of *arsenious oxide* in ammonia reduces mercuric chloroamide in a short time, and the colour changes from white to grey to black owing to the separation of mercury.

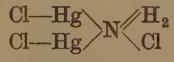
H. Hennell found mercuric chloroamide to be soluble in *hydrocyanic acid*; V. Schwarzenbach found that when heated with a soln. of potassium cyanoplatinite, K_2PtCy_4, it furnishes a soln. of *ammonium cyanoplatinite*, and the yellow chloride of Millon's base, HO.Hg.NH.HgCl; C. Kosmann found that when boiled with twice its weight of *potassium hydrogen oxalate*, carbon dioxide and insoluble mercuric oxalate, $Hg_2C_2O_4$, are formed: $4KHC_2O_4 + 2Hg(NH_2)Cl = 2CO_2 + 2NH_4Cl + 2K_2C_2O_4 + Hg_2C_2O_4$; and when boiled with a soln. of *potassium hydrogen tartrate*, $KH_5C_4O_6$, carbon dioxide is evolved. H. Bauer says that it dissolves without residue in acetic acid of sp. gr. 1·060; and C. Kosmann showed that when the soln. is boiled, mercury and carbon dioxide are formed, while yellow crystals are formed when the soln. is evaporated.

According to V. Schwarzenbach, *ethyl chloride* does not react with mercuric chloroamide at ordinary temp. and press.; but when heated, H. Köhler recognized ethylamine, mercuric and mercurous chlorides among the products of decomposition. *Acetyl chloride* reacts vigorously when heated therewith, forming the corresponding amide. E. Schmidt and L. Krauss obtained by the action of mercuric chloroamide on a soln. of *methyl iodide* in methyl alcohol at room temp. for a long time a double compound of tetramethylammonium and mercuric iodides: $2N(NH_3)_4I.3HgI_2$; and when heated for 2 hrs. in a sealed tube on a water-bath, a compound $N(CH_3)_4I.HgI_2$. F. L. Sonnenschein observed among the products of the action of *ethyl iodide* heated with mercuric chloroamide for many days, (i) an *aqueous solution* of mercuric and ammonium chlorides and a crystalline compound of mercuric chloride with ethylamine hydrochloride; (ii) a heavy dark brown liquid containing the excess of ethyl iodide, from which alcoholic ether extracts a double compound of mercuric iodide with ethyl-, diethyl-, triethylamine hydroiodides, and tetraethylammonium iodide; and (iii) crystals of a double compound of mercuric iodide with tetraethylammonium iodide, $N(C_2H_5)_4I.3\frac{1}{2}HgI_2$ and of $N(C_2H_5)_4I.N(C_2H_4)_2HgI$. M. Zipkin also obtained a double compound, $2N(C_2H_5)_4I.3HgI_2$, by heating a mixture of ethyl iodide and mercuric chloroamide for four months on a water-bath; and after six months' heating, $NH_4I.HgI_2$, together with a little ethylamine and ammonium chloride. S. Hajnoci and M. Löw have studied the action of *methyl iodide* on mercuric chloroamide, and obtained a mixture of $NH_4I.2HgI_2$ or $NH_4Hg_2I_5$, and of mercuric methylammino-iodide, $HgI_2.N(CH_3)H_2$. H. Edhem-Bey found after five weeks' exposure with *chloroform*, mercuric chloroamide forms ammonium and mercuric chlorides, and carbon chloride. Similar results were observed with *iodoform*. R. Wagner found *amyl mercaptan*, $C_5H_{11}.SH$, furnishes a white crystalline compound and mercuric diammino-chloride: $2Hg(NH_2)Cl + 2C_5H_{11}SH = HgCl_2.2NH_3 + (C_5H_{11})_2S_2Hg$, which when dried at 100° and distilled forms mercuric sulphide and amylamine hydrochloride $2(C_5H_{11})NH_2.HCl$. C. Kosmann studied the action of quinine sulphate on mercuric chloroamides.

According to H. Edhem-Bey, *sodium amalgam* attacks mercuric chloroamide with the evolution of ammonia by an exothermal reaction, the mixture becomes brown and then black, and the residue contains sodium chloride, yellow mercuric oxide, and mercury. Similar changes are observed with *alkali hydroxides*. R. J. Kane,

L. Pesci, and H. Gaudechon said that the chloroamide becomes yellow when treated at ordinary temp. with a soln. of potassium or *calcium hydroxide*, half the contained nitrogen is evolved as ammonia, and this fact has been cited in favour of C. F. Rammelsberg and L. Pesci's formula $NH_4Cl.NHg_2Cl$ against R. J. Kane's formula $NH_2.Hg.Cl$, but K. A. Hofmann and E. C. Marburg say that at 130°, the compound loses all its contained nitrogen, as ammonia, when heated with 20 per cent. potassium hydroxide.

There are some compounds which may be regarded as addition products of mercuric chloroamide. For example, N. A. E. Millon's[4] $NH_2Hg_2Cl_3$ may be regarded as a double *mercuric chloride and chloroamide*, $HgCl_2.Hg(NH_2)Cl$; or,



or, according to E. C. Franklin, as a basic mixture, $3HgCl_2.Hg(NH_2)_2$; or, according to E. Balestra as a double dimercuriammonium hydrogen chloride. N. A. E. Millon made this compound by adding aqua ammonia to a large excess of a cold soln. of mercuric chloride; E. Balestra, by adding half as much dil. ammonia to a soln. of mercuric chloride as is needed to precipitate all the mercury; and D. Strömholm, by shaking undried mercuric chloroamide with a 0·5 per cent. soln. of ammonium chloride containing a large proportion of mercuric chloride. H. Gaudechon does not accept the existence of the compound $HgCl_2.H_2NHgCl$; but M. C. C. Holmes made it by heating infusible white precipitate for 1 to 2 hrs. at 100° with a soln. of 0·3 to 1·0 grm. of ammonium chloride in 100 c.c. of water nearly sat. with mercuric chloride. On cooling the filtered soln., a fine white powder separated. The white powder resembles mercuric chloroamide; and it is decomposed into mercuric and ammonium chlorides by washing with cold water. D. Strömholm obtained what he regarded as $2HgCl_2.4N_2HHg_3Cl.H_2O$, by shaking this compound with water; and it is stable in soln. containing a high proportion of mercuric chloride, and a small proportion of ammonium chloride, if but a small proportion of mercuric chloride or a large proportion of ammonium chloride be present, the compound is decomposed; and E. Balestra found that no ammonia is given off when it is treated with potash lye, but is given off copiously when treated with a soln. of ammonium bromide. When hydrogen sulphide acts on the compound in the presence of water, the latter becomes acidic owing to the formation of *mercuric diamminochloroamide*, $HgCl_2.Hg(NH_2)Cl.2NH_3$. According to G. André, crystals of this compound are formed when 20 grms. of yellow mercuric oxide are dissolved in a soln. of 100 grms. of ammonium chloride in 350 grms. of water, and enough dil. ammonia added until the soln. smells strongly. The washed precipitate is dried at 100°. K. Thümmel obtained a white precipitate of a double *mercuric oxychloroamide*, $HgO.HgCl_2.2Hg(NH_2)Cl$, by adding mercuric chloride to an excess of ammonium hydrogen carbonate; when slowly heated to 180° or 200°, it produces a red powder—possibly $2HgCl_2.Hg_3N_2$. K. Thümmel also obtained what he regarded as $3HgO.HgCl_2.2Hg(NH_2)Cl$, as a flocculent white precipitate by adding a mixed soln. of sodium and ammonium hydrogen carbonates to one of mercuric chloride.

Mercuric hydroxychloroamide, HgOH—NH—HgCl, or *mercuric imidohydroxychloroamide* or the *chloride of Millon's base.* It can also be regarded as *dimercuriammonium monoaquochloride*, $Hg:N.HgCl, H_2O$; or as *oxydimercuriammonium chloride*, $O:Hg_2:NH_2Cl$; or as *mercuric oxychloroamide*, $Hg(NH_2).O.HgCl$. R. J. Kane[5] showed that mercuric chloroamide, $Hg(NH_2)Cl$, is hydrolyzed by water, forming mercuric hydroxychloroamide, HgOH.NH.HgCl, the chloride of Millon's base. D. Strömholm, and K. A. Hofmann and E. C. Marburg prepared this compound by digesting the chloroamide with water at 60°–70° for 12 hrs., and washing the product first with hot water, then with alcohol, and finally with ether; it is then dried to constant weight in vacuo. C. F. Rammelsberg, and L. Pesci prepared it by the action of dil. hydrochloric acid on Millon's base, or by the action of a cold

soln. of hydrochloric acid in alcohol. D. Strömholm also hydrolyzed mercuric chloroamide by dissolving 3 grms. of the salt in 70 c.c. of 25 per cent. hydrochloric acid, and filtering the soln. into 500 c.c. of normal sodium hydroxide, and allowing the mixture to stand for some days. R. J. Kane, T. Weyl, and H. Gaudechon also prepared the same compound by the hydrolysis of mercuric diammino-chloride; and E. Balestra hydrolyzed dimercuric dichloroimide, $(HgCl)_2NH$ or $(HgCl)_2N.Hg.N(HgCl)_2$, with a dil. soln. of potassium hydroxide; N. A. E. Millon obtained mercuric hydroxychloroamide by the action of an excess of ammonia on mercuric chloride, and washing the precipitate with hot water; D. Strömholm added 20 c.c. of 8 per cent. ammonia to a soln. of 5 grms. of mercuric chloride in a litre of water, and allowed the mixture to stand with repeated agitation for 6 days at the temp. of the room. G. André used an analogous process. G. André also prepared this compound by dissolving 20 grms. of yellow mercuric oxide in a boiling soln. of 100 grms. of ammonium chloride in 350 grms. of water. The filtered soln. is to be treated with dil. ammonia until it smells strongly of the gas, the precipitate is filtered off, and a large excess of water added to the liquid. H. Gaudechon treated the oxychloride $3HgO.HgCl_2$, or an eq. mixture of the components, with ammonia; and C. Ullgren passed dried ammonia at 150° over the same oxychloride dried at 100°. H. Fürth made the same compound by the action of ammonium chloride on mercuric chloride acetamide, $HgCl_2.CO(CH_3)NH_2$.

Mercuric hydroxychloroamide is usually pale yellow or cream colour, but when pure it is a white powder; that obtained by the aid of potassium is always yellow. R. J. Kane reported that when heated, ammonia, nitrogen, and water are evolved and a sublimate of mercury and mercuric chloride is formed; while C. F. Rammelsberg noted that it loses nearly all its combined water at 200°; D. Strömholm gives 120°. This compound is so stable, said H. Gaudechon, that the combined water cannot be separated without decomposition, for if a little water be expelled by heating it to 130° for 5–6 hrs., the product leaves a residue of mercury when extracted with a soln. of potassium cyanide. K. A. Hofmann and E. C. Marburg say that it is not altered by heating to 120° in a stream of ammonia, or when it is allowed to stand over sulphuric acid. R. J. Kane said it is sparingly soluble in water, and easily soluble in hydrochloric or nitric acid; while H. Gaudechon says it is decomposed by hydrochloric acid, forming mercuric and ammonium chlorides, and C. Ullgren that with hot conc. nitric acid it gives a nitrogen trioxide. D. Strömholm says it is in equilibrium with a 0·15 per cent. soln. of ammonium chloride: $HgOH.NH.HgCl + NH_4Cl \rightleftharpoons H_2O + 2Hg(NH_2)Cl$. L. Pesci found it gives off its nitrogen as ammonia when treated with ammonium bromide; C. F. Rammelsberg obtained similar results with boiling soln. of the alkali chlorides; and C. Ullgren obtained ammonia and mercuric sulphide, by treating it with a soln. of potassium sulphide. E. Balestra obtained mercuric sulphide and a neutral soln. of ammonium chloride by the action of hydrogen sulphide. R. J. Kane found that a boiling soln. of potassium hydroxide gave off no ammonia, and changed only the colour of the salt; E. Balestra confirmed this observation. F. A. Flückiger found that when rubbed up with iodine, mercurous iodide is formed at first, and after some time mercuric iodide; the change is faster if the mixture be warmed with water. M. Zipkin obtained a double salt of mercuric iodide and tetramethyl ammonium iodide by heating it with ethyl iodide for 8 hrs. in a sealed tube on a water-bath. C. F. Rammelsberg noted that a soln. of potassium iodide forms mercuric imidohydroxyiodide, and with an excess of potassium iodide there is a partial decomposition and some ammonia is evolved.

O. Schmieder [6] reported the formation of two *mercuric oxyhydroxychloroamides* which E. C. Franklin formulated as containing $HgO : HgOH.NH.HgCl$ in the ratios 1 : 1 and 1 : 2, but which O. Schmieder regarded respectively as compounds $NH_2(HgO.HgO.Hg)Cl$, and $NH_2(Hg.O.Hg)Cl.NH_2(HgOHgOHg)Cl$. The 1 : 2 compound was made by pouring a dilute hydrochloric acid soln. of hydrated mercuric diammino-sulphate, $HgSO_4.2NH_3.H_2O$, into an excess of dil. potassium hydroxide, and washing the product with hot water; when this substance is boiled with conc.

potash-lye, it forms the 1 : 1 compound. N. A. E. Millon claimed to have made a pale yellow powder of a double compound of *mercuric chloroamide* and *hydroxychloroamide*, which E. C. Franklin formulated $Hg(NH_2)Cl.2(HgOH.NH.HgCl)$, by the prolonged washing of $HgCl_2.Hg(NH_2)Cl$ with water, and by the action of ammonia on a boiling soln. of mercuric chloride—for the latter process G. André recommended pouring 3 vols. of a soln. of 33·875 grms. of mercuric chloride in a litre of water into 2 vols. of a soln. of 4·25 grms. of ammonia in a litre of water; the precipitate remaining after decantation was shaken for 24 hrs. with four more volumes of the ammonia soln., and filtered. E. Balestra failed to prepare this compound by either of N. A. E. Millon's processes, and he regards the product as a mixture of $NH(HgCl)_2$, *i.e.* $NHg_2Cl.HCl$ with $2NHg_2Cl.HgCl_2$. The alternative formula by G. André is $Hg(NH_2)Cl.2(NH_2Hg.O.HgCl)$. G. André also claimed to have made the 1 : 1 and the 2 : 1 salts which E. C. Franklin formulates respectively $Hg(NH_2)Cl.HgOH.NH.HgCl$, and $2Hg(NH_2)Cl.HgOH.NH.HgCl$; the former compound by pouring 6 vols. of a soln. of 4·25 grms. of ammonia in a litre of water into one part of a soln. of 33·875 grms. of mercuric chloride in a litre, and, after standing some hours, washing and drying the precipitate at 110°. The 2 : 1 compound was made by treating one volume of the mercuric chloride with 240 vols. of the ammonia soln. in a similar manner. The 4 : 1 compound, which E. C. Franklin formulates $4Hg(NH_2)Cl.HgOH.NH.HgCl$, was made by N. A. E. Millon by pouring a boiling soln. of mercuric chloride into an excess of aqua ammonia, and washing thoroughly with cold water. E. Balestra regards it as the end-product obtained by thoroughly washing mercuric chloroamide with water.

Dimercuriammonium chloride, or *tetramercuriammonium chloride*, NHg_2Cl, probably has the constitution Hg : N.HgCl, although E. C. Franklin [7] said that it may be also regarded as a basic mixture of mercuric chloride and nitride, or *mercuric chloronitride*, $HgCl_2.Hg_3N_2$. According to H. Gaudechon, this compound has not been isolated, but its existence is made probable by the fact that the corresponding iodide and bromide have been obtained. G. André, K. A. Hofmann and E. C. Marburg, P. C. Ray, and H. Gaudechon believe that the alleged production of this compound is an error. The latter said:

> I have tried to make NHg_2Cl, but all attempts—action of heat, decomposition of double salts, etc.—have not enabled me to isolate it. The impossibility of eliminating the water from the chloride of Millon's first base HgOH.NH.HgCl, or $NHg_2Cl.H_2O$, without decomposition led K. A. Hofmann and E. C. Marburg to infer that this compound possesses a constitution different from $NHg_2Cl.H_2O$, assumed by C. F. Rammelsberg and L. Pesci.

T. Weyl claimed to have made dimercuriammonium chloride by treating Hg : N.HgOH—the second anhydride of Millon's base—with a cold alcoholic soln. of hydrogen chloride; and by the action of liquid ammonia on the oxychloride $3HgO.HgCl_2$; C. F. Rammelsberg obtained it by heating the chloride of Millon's base to 200°; by boiling fusible or infusible white precipitate with water or potash-lye; and by treating Hg : N.HgCl with the calculated quantity of hydrochloric acid; and H. Gerresheim, and C. F. Rammelsberg, by the action of sodium chloride soln. on Hg : N.HgCl. T. Weyl says this compound is a yellow powder which at 300° decomposes suddenly into mercuric chloride, mercury, and nitrogen. It is not decomposed by boiling water; cold dilute hydrochloric acid dissolves it very slowly; cold potash-lye forms potassium chloride and a yellow powder which when washed with alcoholic ammonia and dried, explodes when rapidly heated. Boiling potash-lye was found by L. Pesci, and T. Weyl to decompose it completely, forming ammonia, and mercuric oxide and chloride; soln. of potassium chloride, said T. Weyl, act similarly. L. Pesci showed that an 8 per cent. soln. of ammonium chloride converts it at ordinary temp. into fusible white precipitate, $HgCl_2.2NH_3$. H. Gaudechon reported the formation of four **dimercuriammonium amminochlorides,** $NHg_2Cl.nNH_3$, where n is $\frac{1}{4}$, $\frac{1}{2}$, 1, and 3. C. F. Rammelsberg's, L. Pesci's, and H. Gaudechon's formulæ for infusible and fusible white precipitates represent them as double compounds of dimercuriammonium chloride and ammonium

chloride respectively in the proportions 1 : 1 and 1 : 3, that is, $NHg_2Cl.NH_4Cl$ and $NHg_2Cl.3NH_4Cl$ respectively.

H. Gaudechon said that the so-called *hydrates of dimercuriammonium chloride*, namely, $NHg_2Cl.nH_2O$, where $n=\frac{1}{4}$, $\frac{1}{2}$, and 1, are not different stages in the hydration of this compound, but rather different condensation products, $(NHg_2Cl)_n$, $(NHg_2Cl)_{2n}$, and $(NHg_2Cl)_{4n}$. While the compound $NHg_2Cl.nH_2O$ is preferably regarded as HgOH.NH.HgCl, the compound $NHg_2Cl.\frac{1}{4}H_2O$ is said by H. Gaudechon to be formed by drying $NHgCl.nH_2O$ at 100°; and the compound $NHg_2Cl.\frac{1}{2}H_2O$ was regarded by R. Kane and G. André as having the composition $NHg_2Cl.NH_2Hg.O.HgCl$, while E. C. Franklin assumes it to be a double salt of *dimercuriammonium chloride, and mercuric chlorohydroxyamide*, with NHg_2Cl : HgOH.NH.HgCl in the proportions 1 : 1. G. André made this double salt by mixing 200 c.c. of $\frac{1}{8}N$-mercuric chloride soln. with 150 c.c. of a $\frac{1}{8}N$-potassium hydroxide, and then adding 100 c.c. of a $\frac{1}{2}N$-ammonia—or 150 c.c. of $\frac{1}{8}N$-ammonium chloride soln. The yellow colour disappears after shaking the mixture for half an hour; it is then filtered, washed with cold water, and dried at 110°. H. Gaudechon made it by the action of dil. hydrochloric acid on $NHgOH.H_2O$; by dehydrating HgOH.NH.HgCl with liquid ammonia; and by boiling fusible or infusible white precipitate with water, or, according to L. Pesci, by treating them with a 20 per cent. soln. of potassium hydroxide or sodium carbonate. P. C. Ray hydrolyzed ammonium pentachlorodimercuriate, $NH_4Hg_2Cl_5$, or $NH_4Cl.2HgCl_2$, with dilute potash-lye, and J. Sen similarly hydrolyzed mercuric chloroamide. The product is a pale yellow powder which is very stable. According to H. Gaudechon, the heat of formation is 24·8 Cals., and the heat of hydration 2·0 Cals. P. C. Ray says it loses no appreciable quantity of water at 120°; on further heating J. Sen found it to be decomposed into nitrogen, mercury, and mercurous chloride—a little of the nitrogen may be given off as ammonia. If allowed to stand for several days in contact with water at 15°, H. Gaudechon could detect no transformation into $NHg_2Cl.H_2O$, nor indeed by heating to 100° for 100 hrs. G. André also prepared what E. C. Franklin formulated as the 1 : 2 double compound $Hg_2NCl.2(HgOH.NH.HgCl)$, and G. André as $Hg_2NCl.2(NH_2Hg.O.HgCl)$ or as $3Hg_2NCl.2H_2O$, by pouring 200 c.c. of $\frac{1}{8}N$-mercuric chloride into 400 c.c. of ammonia, and washing the precipitate rapidly by decantation with a small quantity of water. The precipitate was then shaken for 1½ hrs., filtered, washed, and dried at 110°. He also prepared the same compound by adding an ammoniacal soln. of potassium hydroxide into $\frac{1}{8}N$-mercuric chloride soln.

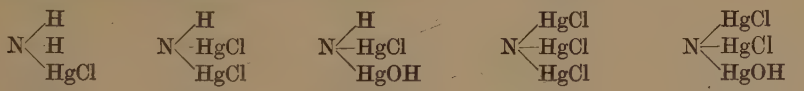
G. André reported what may be regarded as triple compounds of mercuric chloroamide and hydroxychloroamide with dimercuriammonium chloride, $Hg(NH_2)Cl$: Hg_2NCl : HgOH.NH.HgCl in the molecular proportions 1 : 1 : 1; 1 : 2 : 1, and 2 : 1 : 1.

Mercuric dichloroamide, $(HgCl)_2NH$.—E. C. Franklin[8] also suggests that this compound may be really a basic mixture of mercuric chloride, $HgCl_2$, and mercuric imide, HgNH. E. Balestra regards it as a complex acid or double compound of hydrochloric acid and dimercuriammonium chloride, $NHg_2Cl.HCl$, just as the compound $HgCl_2.NH_2HgCl$ can be regarded as $NHg_2Cl.2HCl$; and NH_4HgCl_5 or $NH_4Cl.2HgCl_2$, as $NHg_2Cl.4HCl$. E. Balestra made this compound by adding to 200 c.c. of a boiling 7 per cent. soln. of mercuric chloride, half as much ammonia as is necessary to make the soln. neutral to litmus. The amorphous yellow powder is dried in air; when suspended in water, it is decomposed by hydrogen sulphide, and the water acquires a strong acid reaction. It develops ammonia when digested with ammonium bromide, but not with potash-lye.

Mercuric tetrachloroamide, $(HgCl)_2N.Hg.N(HgCl)_2$.—E. C. Franklin considers the possibility of this substance being a basic mixture of mercuric chloride, $HgCl_2$, and mercuric nitride, Hg_3N_2, or *mercuric chloro-nitride*. It can be regarded as a double salt of dimercuriammonium and mercuric chloride, $2NHg_2Cl.HgCl_2$; or of $HgCl_2(Hg : N.HgCl)_2$. E. Mitscherlich found it remaining in small red crystalline

plates resembling red mercuric oxide. When infusible white precipitate, NH_2HgCl, is carefully heated in a retort, immersed in a bath of fusible metal, until the ammonia is all driven off, and the mercuric monamminochloride, $HgCl_2.NH_3$, and mercuric chloride begin to sublime : $6Hg(NH_2)Cl=3NH_3+Hg(NH_3)Cl_2+(HgCl)_2$: N.Hg.N : $(HgCl)_2$. P. C. Ray made it as a yellow precipitate by adding potash-lye carefully, not in excess, to a boiling soln. of ammonium pentachlorodimercuriate, $NH_4Cl.2HgCl_2$. H. Gaudechon prepared it by the action of hydrochloric acid on the chloride of Millon's base ; and by mixing a hot conc. soln. of mercuric chloride with an equi-molar quantity of ammonia, washing the precipitate free from chlorine, and drying at 100°. E. Mitscherlich says that this compound decomposes into nitrogen, mercury, and mercurous chloride when heated above the boiling point of mercury ; it is scarcely affected by water at 18°, and it dissolves in boiling hydrochloric acid, forming ammonium and mercuric chlorides ; boiling sulphuric acid decomposes it in an analogous manner ; it is not dissolved or decomposed by boiling nitric acid, dil. sulphuric acid, or by alkalies. H. Gaudechon says that when treated with aqua ammonia, cold or hot, a mixture of $Hg(NH_2)Cl$ and HgCl.NH.HgOH is formed.

Mercuric trichloroamide, $N(HgCl)_3$.—It will be observed that the mercuric chloroamides can be graphically represented by the formulæ :



H. Vittenet reported that when equal parts of ammonium and mercuric chlorides are dissolved in tap-water, there slowly forms a precipitate, which is at first white and has the composition $N(HgCl)_2$, but on further standing gradually becomes yellow. The production of this substance was traced to the presence of acid carbonates in the water, and its formation was found to be inhibited by previously boiling the water. When the two salts are dissolved in distilled water to which sodium hydrogen carbonate or carbonate has been added, the precipitate formed is white and has the composition of a double salt with ammonium chloride, $N(HgCl)_3.3NH_4Cl$. H. Vittenet represents the reactions by the equations : $3HgCl_2+4NH_4Cl+4NaHCO_3=N(HgCl)_3.3NH_4Cl+4NaCl+4CO_2+4H_2O$; and $3HgCl_2+4NH_4Cl+2Na_2CO_3=N(HgCl)_3.3NH_4Cl+4NaCl+2CO_2+2H_2O$. The compound $N(HgCl)_3.3NH_4Cl$ gradually becomes yellow when washed with water ; the final product is bright yellow, and has approximately the composition required for **mercuric dihydroxyhypochloroamide,** $N(Hg.OH)_2.Hg.OCl$. **Mercuric hydroxydichloroamide,** $N(HgCl)_2.HgOH$, is formed as an intermediate product, $2N(HgCl)_3+O_2=2N(HgCl)_2HgOCl$; and $N(HgCl)_3+H_2O=HCl+HgOH.N(HgCl)_2$. The formation of these precipitates in soln. used in antiseptic baths leads to a diminution of efficiency, and it is suggested that in preparing these, the water should first be boiled or the ammonium chloride should be replaced by sodium chloride ; with either of these precautions, no precipitation occurs.

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§ 17. Hydroxylamine and Hydrazine Compounds of Mercuric Chloride

L. Crismer [1] has prepared chlorides of barium, zinc, cadmium, cobalt, and manganese with hydroxylamine of crystallization of the general formula $MCl_2.(NH_2OH)_2$, but W. Feldt failed to obtain a mercuric salt analogous with the sulphates of manganese, cobalt, and nickel prepared in conjunction with R. Uhlenhuth. In an attempt to prepare compounds with hydroxylamine analogous with

the amminomercuriates, W. F. C. Dresler and R. Stein found that hydroxylamine reduced mercuric oxide to free mercury; W. Lossen found that mercuric chloride was rapidly reduced; but M. Adams prepared several compounds of hydroxylamine with mercuric salts by varying the temperature and solvent.

Freshly precipitated mercurous chloride is very slightly soluble in hydroxylamine hydrochloride, but no combination has been observed; when mercurous chloride is boiled with hydroxylamine and methyl alcohol in a flask fitted with a reflux condenser, the mercurous salt is slowly reduced; the reduction proceeds much more slowly in the cold. The presence of hydroxylamine hydrochloride raises the solubility of mercuric chloride in water or in alcohol, and white crystals of **mercuric hydroxylamine hydrochloride,** $HgCl_2(NH_2OH).HCl$, are obtained by mixing a mol each of mercuric chloride and hydroxylamine hydrochloride in as little water as possible, and evaporating the soln. over calcium chloride. The salt is so very soluble in alcohol and in water that it is difficult to purify; it is less soluble in ether. A mixed soln. of mercuric chloride and hydroxylamine hydrochloride in excess of the proportion 1 : 1, when evaporated, furnishes crystals of the former salt, and if less than this proportion be used, hydroxylamine hydrochloride separates out. If other salts are formed they dissociate on conc. and cannot be obtained in this way. The low solubility of hydroxylamine hydrochloride in ether is not favourable to the production of double salts with an ethereal soln. of mercuric chloride; and although the solubility of the hydrochloride is augmented if alcohol or ligroin be present, no definite double salt could be obtained.

If free hydroxylamine be present, the case is different, for whenever mercuric chloride is present in soln. with an excess of hydroxylamine and its hydrochloride, **dimercuric decahydroxylamine hydrochloride,** $2HgCl_2.5(NH_2OH)_2.HCl$, is formed. This salt is the most easily prepared of the mercuric hydroxylamine salts, and M. Adams indicates several modes of preparation—*e.g.* the action of an alcoholic soln. of hydroxylamine hydrochloride on freshly prepared mercuric oxide suspended in alcohol at about −10°; etc. The salt is soluble in water at ordinary temp., and is gradually reduced to mercurous chloride; it is soluble in alcohol, ether, and hydrochloric acid. The presence of a trace of alkali hastens the decomposition —*e.g.* mercuric oxide at −10° slowly decomposes the salt. When aq. ammonia is added to the aq. soln. a white precipitate is formed which gradually blackens in the cold, rapidly when heated.

M. Adams prepared **mercuric dihydroxylamine chloride,** $HgCl_2(NH_2OH)_2$, by adding a cold alcoholic soln. of hydroxylamine, drop by drop, with constant agitation, to a soln. of mercuric chloride in absolute alcohol cooled down to −10°, or by adding free hydroxylamine in a similar manner, to an alcoholic soln. of hydroxylamine hydrochloride with four times its weight of mercuric chloride. White microscopic crystals soon separate out; they are contaminated with mercurous chloride and combined hydroxylamine hydrochloride. The washed crystals are purified by dissolving them in absolute alcohol to which a trace of hydroxylamine hydrochloride has been added, and long white acicular crystals separate from the soln. The salt is fairly soluble in methyl or ethyl alcohol from which soln. it is precipitated by ether; it is insoluble in ether. On standing in absolute alcohol there is much reduction, the action is more rapid in warm soln. than in the cold. The salt is readily soluble in an aq. soln. of hydroxylamine hydrochloride, and an aq. soln. of the salt is much more stable if a little hydroxylamine hydrochloride is present—presumably a double salt is formed. Sodium hydroxide rapidly decomposes the salt; if ammonia be added to an alcoholic soln. or an aq. soln. mixed with hydroxylamine hydrochloride, a white precipitate is formed which becomes black on standing in the cold, or immediately on warming.

In the preceding preparation, if a mol of mercuric chloride with two of hydroxylamine hydrochloride be employed, the resulting crystals, when purified by recrystallization from methyl alcohol, have the composition **mercuric tetrahydroxylamine dihydrochloride,** $HgCl_2(NH_2OH)_2(NH_2OH.HCl)_2$. If a mol each of mercuric and

hydroxylamine hydrochlorides be employed, crystals of **mercuric tetrahydroxylamine hydrochloride,** $HgCl_2(NH_2OH)_4HCl$, are formed. Both salts are soluble in methyl or ethyl alcohol; they are unstable in aq. soln.; and in the presence of alkalies. The former salt appears to be the most stable of the mercuric hydroxylamine salts, and it can be recrystallized unchanged from methyl alcohol; the latter salt is largely reduced under similar conditions, furnishing mercuric chloride and mercuric dihydroxylamine chloride.

T. Curtius and F. Schrader [2] found that mercuric chloride is reduced by hydrazine dihydrochloride, forming a yellow precipitate which soon turns grey, and cannot be isolated. Hydrazine dihydrochloride precipitates mercurous chloride from soln. of mercurous nitrate. K. A. Hofmann and E. C. Marburg prepared hydrazine derivatives of mercuric chloride which they believe to be analogous with the mercuri-ammonium compounds. When mercuric chloride and hydrazine hydrate are brought together in soln. in alcohol and ether, **mercuric hydrazine chloride,** $N_2H_4HgCl_2$, is precipitated; it is moderately stable when dry, but unstable when moist, and decomposes rapidly when heated, but does not explode. When this compound is shaken with water, or when sodium acetate is added to the mixed aq. soln. of hydrazine sulphate and mercuric chloride, an unstable yellow **mercuric hydrazidochloride,** $N_2H_2Hg_2Cl_2$, is produced which explodes when heated or struck, and rapidly decomposes when moist, nitrogen being evolved and mercury and calomel left. It is readily soluble in hydrochloric acid, but always leaves a small residue of calomel. Alkalies decompose it rapidly. These two compounds appear to be strictly analogous to the fusible and infusible white precipitates, $2NH_3$, $HgCl_2$, and NH_2HgCl. Lustrous tabular crystals of **mercuric hydrazine hydrochloride,** $HgCl_2.N_2H_4.HCl$, were made by treating the hydrazidochloride with chlorine in the presence of carbon tetrachloride; it is also formed from its components in the presence of an excess of mercuric chloride. The m.p. is 157°. T. Curtius and F. Schrader found that **mercuric dihydrazine hydrochloride,** $HgCl_2.2N_2H_4.HCl$, is readily soluble, and may be recrystallized from water or alcohol. It forms well-developed six-sided prisms, which become opaque in the air, and melt at 178° without decomposing.

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§ 18. Mercurous Bromide

There are two bromides of mercury—mercurous bromide, HgBr; and mercuric bromide, $HgBr_2$. A. J. Balard [1] found that mercury united with bromine at ordinary temp., and W. A. Shenstone showed that thoroughly dried bromine unites with dry mercury. The product is mercurous bromide if the mercury be in excess, and mercuric bromide if the bromine be in excess. M. Berthelot showed that at ordinary temp. hydrogen bromide and hydrogen gases slowly react with mercury, forming mercurous bromide; the action is faster if the temp. be raised, and, according to G. F. Bailey and G. J. Fowler, it is faster than with hydrogen chloride.

A. J. Balard precipitated mercurous bromide by adding potassium bromide to a soln. of mercurous nitrate in dil. nitric acid (1 : 100), and, add H. Saha and K. N. Choudhuri, the precipitate is first washed by decantation with light excluded, then washed on a filter, and dried over calcium chloride. R. Varet dried the

precipitate at 105°. O. Henry used other soluble bromides in place of the potassium salt. A. Stroman prepared the same salt by adding bromine, bromine water, or an alcoholic soln. of bromine to a soln. of mercurous nitrate. C. Löwig prepared mercurous bromide by sublimation from a mixture of a gram-atom of mercury, and a mol of mercuric bromide. According to A. Lottermoser, the preparation and properties of colloidal mercurous bromide resemble those for mercurous chloride.

The salt prepared by A. J. Balard's process is a white powder resembling calomel; that prepared by C. Löwig's process is a white fibrous mass; I. Guareschi obtained the salt by sublimation in small colourless crystals; and A. Stroman said that white tetragonal plates can be obtained by cooling a hot soln. of the salt in mercurous nitrate. C. J. B. Karsten found the sp. gr. to be 7·307. O. Henry noted that the white salt becomes yellow when heated, and the white colour is restored on cooling; the salt also melts—according to T. Carnelley—at about 405°, and, according to C. Löwig, it volatilizes without decomposition at a red heat. A. Stroman noted that volatilization occurs at 340° to 350°. E. Beckmann found the lowering of the f.p. of mercuric bromide by the addition of mercurous bromide agreed with the formula Hg_2Br_2. E. Mitscherlich's value for the vapour density, air unity, is 10·14, the corresponding mol. wt. is near that required for HgBr, or, as in the analogous case of mercuric chloride, with that required for partial or complete dissociation into $HgBr_2+Hg$. J. Thomsen's value [2] for the heat of formation from its elements is $(2Hg, Br_2)$, 68·29 Cals.; M. Berthelot gives $Hg_{solid}+Br_{solid}=HgBr_{solid}+35$ Cals.; and R. Varet, $2Hg_{liq.}+Br_{2liq.}=Hg_2Br_{2solid}+49·1$ Cals.; $2Hg_{liq.}+Br_{2gas}=Hg_2Br_{2solid}+56·4$ Cals. J. Thomsen also gives $(Hg_2O, 2HBr_{gas})=77·57$ Cals.; and $(2HgNO_{3aq.}, 2KBr_{aq.})=31·94$ Cals. R. Varet gives $Hg_2O+2HBr_{aq.}=Hg_2Br_{2solid}+H_2O+38·76$ Cals.; and $HgBr_{2solid}+Hg_{liq.}=Hg_2Br_{2solid}+8·5$ Cals. The free energy of formation at 18°, calculated by M. de K. Thompson, is 42·8 Cals., and the total energy, 49 Cals. F. Braun obtained a transformation of 41 to 46 per cent. of the thermal into electrical energy with gaseous or liquid bromine. According to M. Berthelot, the displacement of the bromine by chlorine develops 5·6 Cals.

According to O. Wolff,[3] the vapour of mercurous bromide has an orange fluorescence in ultra-violet light; and, according to J. A. Wilkinson, the vapour is luminescent. A. Stroman found mercurous bromide to be far less sensitive to light than mercurous iodide. C. Fritsch has measured the conductivity of pressed plates of mercurous bromide. According to H. M. Goodwin, the electromotive force of the cell Hg | Hg_2Br_2, $\frac{1}{10}N$-KBr | $\frac{1}{10}N$-KCl, Hg_2Cl | Hg is 0·1338 volt at 17°; according to S. Bugarsky, for Hg | Hg_2Br_2, $\frac{1}{100}N$-KBr | N-KNO_3 | $\frac{1}{100}N$-KCl, Hg_2Cl_2 | Hg the e.m.f. is $\epsilon=0·2149$ volt at 43·3°; 0·1285 volt at 18°; and 0·1311 at 0°; and $d\epsilon/d\theta=-0·000144$. The calculated free energy is 297 cals., the bound energy 964 cals., and the total energy 3935 cals.—the observed heat of the reaction is 4010 cals. For Hg | Hg_2Br_2, $\frac{1}{100}N$-KBr | N-$KC_2H_3O_2$ | N-$KC_2H_3O_2$, $Hg_2(C_2H_3O_2)_2$ | Hg the e.m.f. is $\epsilon=0·2474$ volt at 18·5°; and 0·2667 volt at 0°, and $d\epsilon/d\theta=-0·00104$. The calculated free energy is 5717 cals., the bound energy 6906 cals., the total energy 12,620 cals.—the observed heat of the reaction is 1200 cals. According to R. Behrend, a soln. of mercurous bromide in $\frac{1}{10}N$-KBr contains a milligram of Hg-ions per 1300 litres. On the inexact assumption that the whole of the dissolved mercury is present as $Hg^{\cdot\cdot}$-ions, R. Abegg calculated from the measurements of C. Immerwahr and F. Jander, that soln. of mercurous bromide in potassium bromide of conc. N contain complexes of conc. C, and the ratios of the conc. of the complex to the free ions is K:

N	1·0	1·5	2·0	3·0
C	0·00805	0·0176	0·0343	0·0783
K	0·00805	0·0119	0·0172	0·0268

Mercurous bromide is odourless and tasteless. It was formerly considered to be insoluble in water, but more refined measurements have shown M. S. Sherrill [4]

that a litre of water dissolves 7×10^{-8} grm. per litre; G. Bodländer, $9{\cdot}1\times10^{-7}$; M. de K. Thompson, $1{\cdot}4\times10^{-7}$; and L. Rolla, 3×10^{-7}. As in the analogous case of mercurous chloride, mercurous bromide is slowly converted by water into mercuric bromide. According to R. Abegg, the conc. of the mercuric chloride in a sat. soln. of mercurous chloride is $2{\cdot}4\times10^{-6}$ mols per litre. A. Mailfert said that ozone converts mercurous bromide into mercuric bromide and oxybromide. According to T. Fischer and H. von Wartenberg, if a mixture of mercuric oxide, mercurous bromide, and water be heated in a sealed tube for 48 hrs. at 180°, and the unchanged mercuric oxide and mercurous bromide be removed by levigation, dark red rhombic plates of **mercurous oxybromide** are formed, HgO.HgBr, and they behave towards alkalies and acids like a mixture of the two components. According to I. Guareschi, when a dry mixture of iodine and mercurous bromide is heated bromine and mercuric iodide are formed; but with the gradual addition of iodine to mercurous bromide, mercuric bromo-iodide is formed. According to A. Stroman, dil. or hot fuming hydrochloric acid blackens mercurous bromide owing to the separation of mercury, mercuric chloride passes into soln. According to L. Mailhe, the action of alkali chlorides on mercurous bromide resembles their effect on mercurous chloride. A. Ditte noted that mercurous bromide is decomposed by a conc. soln. of potassium cyanide or potassium iodide, forming a double salt and mercury. C. Löwig found that a boiling soln. of ammonium chloride or bromide decomposes mercurous bromide, forming the mercuric salt and mercury, but a cold soln. of ammonium chloride was reported by G. C. Wittstein to have no perceptible action. G. C. Wittstein also found that a cold soln. of ammonium carbonate or succinate has no appreciable action, while a hot soln. easily dissolves mercurous bromide, leaving behind a grey powder which is presumably metallic mercury; the same observer found that mercurous bromide is not perceptibly soluble in cold or boiling soln. of ammonium sulphate or nitrate. A. Stroman found that fuming nitric acid of sp. gr. 1·42 dissolves mercurous bromide after a prolonged heating; and it is completely dissolved by hot conc. sulphuric acid with the evolution of sulphur dioxide. Alkali hydroxides were found by C. Löwig to yield potassium bromide and mercurous oxide. The action of hydrocyanic acid on mercurous bromide, says E. Esteve, resembles its action on mercurous chloride. I. Guareschi observed no evolution of bromine when mercurous bromide is heated with 25 to 50 per cent. soln. of chromic acid. A. Naumann found mercurous bromide to be insoluble in benzonitrile. C. Löwig found that when mercurous bromide is heated with phosphorus, mercurous bromide is converted into phosphorous bromide, and mercury phosphide. According to C. F. Rammelsberg, when mercurous bromide is treated with cold aqua ammonia, and washed with water containing ammonia, it leaves a grey powder which contains globules of metallic mercury, and when heated yields a sublimate of mercury and of mercurous and mercuric bromides. According to A. Stroman, some ammonium bromide is formed at the same time, and, according to H. Saha and K. N. Choudhuri, the black residue is a mixture of finely divided mercury and of $HgO.NH_2HgBr.2H_2O$—dihydrated mercuric oxybromide. J. G. F. Druce formulated the reaction $2NH_4OH+Hg_2Br_2=NH_2HgBr+Hg+NH_4Br+2H_2O$.

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§ 19. Mercuric Bromide

This compound was formed by A. J. Balard in 1826, by the action of an excess of bromine on mercury. C. W. Easley and B. F. Braun [1] conducted the process by passing a stream of purified dry nitrogen through an apparatus resembling that depicted in Fig. 22, after purified mercury has been introduced into the bulb by

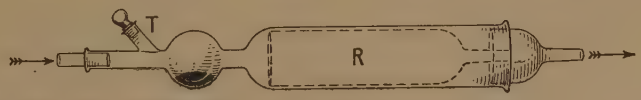

Fig. 22.—The Preparation of Mercuric Bromide—C. W. Easley and B. F. Braun.

means of a funnel through the tubular *T*. When the air was expelled, the nitrogen was passed through liquid bromine before it entered the apparatus. The bulb was heated to 300°, the mercury in the bulb was converted into the bromide and sublimed into the receiver *R*, which was kept at a temp. of 235°. Nitrogen alone was passed through the apparatus during the sublimation. The heating was done by means of air ovens with asbestos walls. Beautiful needle-like crystals of mercuric bromide collected in the receiver.

C. Löwig, L. Larine, and W. Reinders prepared this same compound by the action of an excess of hot bromine water on mercury ; T. Hjortdahl used alcohol in place of water, and J. Schröder used pyridine. Bromine was added so long as the supernatant liquor was decolorized, the excess of bromine was boiled off, and the filtered liquid evaporated for crystallization. W. L. Hardin sublimed the thoroughly dried crystals from a porcelain crucible into a glass tube.

C. Löwig made the same salt by the action of hot hydrobromic acid on mercuric oxide ; and by sublimation from a mixture of mercuric sulphate and potassium bromide—O. Henry says the product always contains some mercurous bromide. C. Löwig also evaporated a mixed soln. of mercuric nitrate and potassium bromide so long as mercuric bromide crystallized out and purified the product by soln. in alcohol ; and W. Sievers agitated an excess of bromine with a soln. of mercuric nitrate of sp. gr. 1·197 : $Hg(NO_3)_2+2Br_2+2H_2O=HgBr_2+2HOBr+2HNO_3$; the product was dissolved in a hot soln. of mercuric nitrate of the same sp. gr., the soln. was cooled, and the crystals washed first with water acidified with nitric acid, then with water, and finally dried. R. Wagner made this salt by the action of bromine water or of a soln. of bromine in hydrochloric acid on mercuric sulphide. A. Lottermoser prepared colloidal mercuric bromide like he prepared colloidal mercuric chloride.

The properties of mercuric bromide.—The **crystals** of mercuric bromide obtained from aq. soln. are lustrous white plates ; and from alcoholic soln. white

needles. According to W. J. Luczizky,[2] the rhombic bipyramidal crystals have the axial ratios $a:b:c=0{\cdot}6826:1:1{\cdot}7953$; these crystals are not isomorphous with those of mercuric chloride, and therefore a second rhombic modification isomorphous with mercuric chloride is assumed to exist. This was confirmed by W. J. Luczizky, who obtained from alcoholic soln. the rhombic form of mercuric bromide. The ordinary form of mercuric bromide is isomorphous with the yellow form of mercuric iodide which is stable at the higher temp. Isomorphous mixtures of these two salts are readily formed, and the combination $HgI_2.HgBr_2$, or HgIBr, is particularly stable, and was assumed by A. Oppenheim to be a compound. J. S. van Nest, therefore, assumed that mercuric bromide is trimorphous, and that the third modification is isomorphous with the low temp. tetragonal form of mercuric iodide—*vide* Fig. 25 and the bromochlorides—but W. Reinders could not find any sign of a transition point at temp. down to −83·5°.

Numbers ranging from F. W. Clarke's [3] 5·7379 (18°) to C. J. B. Karsten's 5·9202 have been published for the **specific gravity** of mercuric bromide. The mean of three determinations by J. S. van Nest is $6{\cdot}064\pm0{\cdot}05$ (20°), and W. Ortloff's value for the **molecular volume** is 62·69; W. Biltz gave 59·4 assuming the sp. gr. to be 6·064. According to K. Beck, the sp. gr. of the molten salt (water at 18° unity) is 5·26 at 240°, 5·24 at 258°, and for $\theta°$ between 240° and 340° E. B. R. Prideaux gives for the sp. gr. $5{\cdot}116-0{\cdot}00338(\theta-240)$. According to E. B. R. Prideaux, 100 vols. of the elements mercury and bromine, $Hg+Br_2$, on combination at 760 mm. become 107·4 vols.; and the sp. gr. at 200 mm. press. 5·037 falls to 4·840 at 860 mm., and to 4·821 at 860 mm. O. Grotrian found the sp. gr. of soln. with 0·223 per cent. of the salt is 1·0007 (17·99°), and 1·0001 (20·87°), and for 0·422 per cent. soln. 1·0025 (18·19°) and 1·0020 (20·40°). The **viscosities** of the molten salt were found by K. Beck to be 3·698 (240°), 3·321 (2·47°), and 2·208 (258°), when water at 25° is unity.

The reported numbers for the **melting point** vary from the 222° of J. S. van Nest [4] the 222°–223° of A. Oppenheim and to the 244° of T. Carnelley. F. M. G. Johnson found a break in the vap. press. curve corresponding with the m.p. 236°, which may also be regarded as the best representative value of determinations by E. Beckmann, W. Reinders, K. Beck, P. Niggli, and C. Sandonnini. F. M. G. Johnson gives 318° (760 mm.) for the **boiling point**; T. Carnelley and W. Hampe give 319°; and F. Freyer and V. Meyer, 335°. As with mercuric chloride, E. Esteve noted that some salt is lost by volatilization during the evaporation of an aq. soln. on a water-bath and drying at 100°. A. J. Balard, and C. Löwig noted that mercuric bromide melts and is volatile, and W. Sievers added that it does not simultaneously decompose. H. Arctowsky found it to be volatile even at ordinary temp., and that after five hours' heating it lost 0·0101 grm. at 79·5°; 0·0182 grm. at 105°; and 0·0732 grm. at 126·5°. O. Sulc found the finely powdered salt lost 4·1 per cent. in weight at 101·5°. The **vapour pressure** of mercuric bromide, p mm. of mercury, has been measured by F. M. G. Johnson, E. B. R. Prideaux:

	162°	206°	229°	233°	238°	247°	255°	290°	318·5°
p	3	29	73	88	106	136	174	413	764

There is a break at the m.p., 236°, and at the b.p. E. Wiedemann, K. Stelzner, and G. Niederschulte give 0·045 mm. at 90°; 0·18 mm. at 110°; 0·72 mm. at 130°; and 2·30 mm. at 150°. The **heat of vaporization** calculated by Clausius' formula is 14·24 cals., between 760 mm. and 800 mm. **Trouton's constant** is $Q/T=24{\cdot}13$; and W. Ramsay and S. Young's ratio $T_1/T_2=1{\cdot}043$ (750 to 450 mm.). E. Beckmann gave for the **latent heat of fusion,** 13·9 Cals. per gram. The **critical temperature** was found by L. Rotinjanz and W. Suchodsky to be 1011° K. in agreement with the value 1013° K. calculated from T. E. Thorpe and A. W. Rucker's formula. C. M. Guldberg's ratio $T_b/T_c=0{\cdot}587$, where T_b denotes the b.p. and T_c the critical temp. in absolute degrees. H. Rassow gave 738° for the critical temp. M. Prud'homme, and E. van Aubel studied the relation between the critical temp., the b.p., and the m.p. According to E. Mitscherlich,

the **vapour density** is 12·16 (air unity) or 351 (H_2=2), when the theoretical value for $HgBr_2$ is 350. V. Borelli found the mol. wt. calculated from the lowering of the f.p. of water is 370, corresponding with $HgBr_2$ (360); M. Hamers, from the raising of the b.p. of soln. in ethyl acetate, found 345·7; H. Steiner, in methyl acetate, 293·4 to 343·4—representing a possible ionization of 12·5 per cent. or a possible reaction with the solvent; A. Werner and M. Stephani, in ethyl sulphide, 352; and J. Schröder, in pyridine, 418. P. Walden and M. Centnerszwer said that the calculated mol. wt. in dil. pyridine soln. is normal and increases with increasing conc. E. Beckmann found mercurous bromide has a mol. wt. agreeing with Hg_2Br_2 in fused mercuric bromide. F. Olivari measured the cryoscopic constants of mercuric bromide.

R. Varet[5] estimates the **heat of formation** of mercuric bromide from the liquid elements to be 40·6 to 40·7 Cals., and from liquid mercury and gaseous bromine, 47·9 Cals.; J. Thomsen gives 50·55 Cals. (bromine liquid); and W. Nernst, 40·5 Cals. The **free energy** of formation from the ions is 23·52 cals., according to M. S. Sherrill; and M. de K. Thompson gave −37,300 cals. M. Berthelot gives ($HgBr$, Br_{solid}), 17·6 Cals.; and for the action of hot aq. hydrobromic acid on HgO, 26·4 Cals.; 23·0 Cals. in soln.; and for a soln. of one eq. of HgBr in 40 litres at 12°, 2HBr+HgO (precipitated), 27·4 Cals. for HgBr dissolved, and 30·8 Cals. for crystalline $HgBr_2$. M. Berthelot gives for the heat of soln. −3·4 Cals.

J. A. Wilkinson[6] said that the vapour of mercuric bromide has an orange **fluorescence.** B. O. Peirce[7] found the **emission spectrum** of mercuric bromide gave a band with a mid-point near 5000. C. Sheard and C. S. Morris found a continuous spectral band with mercuric bromide between 5075 and 4912. The **magnetic susceptibility** was found by S. Meyer to be $0·24\times10^{-6}$ units of mass, and $0·15\times10^{-6}$ units of vol. C. Fritsch[8] measured the **electrical conductivity** of a pressed plate. W. Hampe says that melted mercuric bromide conducts better than mercuric chloride under similar conditions; the decomposition is not apparent, but there is a feeble polarization current. The sp. electrical conductivity in soln. of molten aluminium bromide at 99·5° rises from $0·01\times10^{-5}$ with 1·38 per cent. soln. to $0·88\times10^{-5}$ with 5·52 per cent. soln.; $41·89\times10^{-5}$ with 8·14 per cent. soln.; and to $979·9\times10^{-5}$ with 27·15 per cent. soln.

O. Grotrian measured the sp. electrical conductivities and found that aq. soln. with 0·223 per cent. of mercuric bromide at 18·09° and 25·92° had the respective sp. conductivities $0·15\times10^{-8}$ and $0·19\times10^{-8}$; and a 0·422 per cent. soln. at 18·01° and 25·94°, the respective sp. conductivities $0·24\times10^{-8}$ and $0·30\times10^{-8}$. H. Ley and H. Kissel found the mol. conductivity of a soln. with a mol of the salt in 128 litres of water to be 1·3, and they add that the only compounds of bivalent mercury which show a tendency to ionization are those in which the metal is directly united with oxygen—thus, the mol. conductivities of the chloride and bromide are low, while the conductivity of the cyanide is even lower. According to H. N. Morse, the ionization constants are: $[Hg^{\cdot\cdot}][Br']=0·4\times10^{-9}[HgBr^{\cdot}]$; $[HgBr^{\cdot}][Br']=5·0\times10^{-9}[HgBr_2]$; $[Hg^{\cdot\cdot}][Br']^2=2·0\times10^{-18}[HgBr_2]$; and $[Hg^{\cdot\cdot}][HgBr_2]=0·08[HgBr]^2$. M. S. Sherrill gives for the complexes $[HgBr_4'']=4·3\times10^{21}[Hg^{\cdot\cdot}][Br']^4$; and $[HgBr_4'']=2·8\times10^4[HgBr_2][Br']^2$; and for the conc. of $HgBr_2$, $1·7\times10^{-2}$; $[HgBr^{\cdot}]$, and $[Br']$, $0·9\times10^{-5}$; for $[Hg^{\cdot\cdot}]$, $0·9\times10^{-9}$; and for $[HgBr_4'']$, $2·8\times10^{-8}$. H. N. Morse measured the **transport numbers**. According to W. Matthies, the **glow discharge** in the vapour has a stronger cathode fall than with the vapour of mercuric chloride.

J. L. Lassaigne[9] found the **solubility** of mercuric bromide to be 1·05 per cent. at 9°, and 16·7 to 25 per cent. in boiling water. L. Larine gives the solubility as about 0·8 per cent. at ordinary temp., and 8 to 9 per cent. at 100°. W. Herz and W. Paul say that at 25°, water dissolves 0·017 mol per litre—a similar result was obtained by F. Jander, M. S. Sherrill, and R. Abegg. According to H. N. Morse, at ordinary temp. a litre of water dissolves about 4 grms. of the salt, and, according to H. Gaudechon, 5 to 6 grms. A. Vicario said that if a hot soln. be cooled, more mercury will be present than if prepared cold, because boiling water decomposes

mercuric bromide into hydrobromic acid and a yellow oxybromide, and mercuric bromide is more soluble in a dil. soln. of hydrobromic acid than in water. C. Löwig also noted the increased solubility of the salt in hydrochloric or hydriodic acid; F. Jander made a similar observation with respect to soln. of sodium or potassium bromide—if S denotes the solubility of mercuric bromide in water, at 25°, and S_0 the solubility in soln. of alkali chloride containing C mols per litre:

C . .	0·1	0·5	1·0	2·0	3·0	4·0
$S-S_0$(KCl)	0·071	0·342	0·691	1·390	2·079	2·322
$S-S_0$(NaCl)	0·0697	0·398	0·798	—	1·864	—

It is assumed that the complexes $KHgBr_3$ and $NaHgBr_3$ are respectively formed—*q.v.* R. Abegg calculated the equilibrium constants for soln. of these complexes. M. S. Sherrill found that additions of from a half to one mol of potassium bromide raised the f.p. of soln. of mercuric bromide up to a maximum, and the further additions had very little effect on the f.p. of the soln. up to saturation. These phenomena are taken to mean that anionic complexes $HgBr_4'$ are at first formed, and this is later followed by the addition of more bromide to form a higher complex Hg_2Br_6''. R. Varet further added that the heat of combination of mercuric bromide with the bromides of other metals is approximately of the same order of magnitude for the same series of double salts. W. Herz and W. Paul obtained confirmatory results with soln. of bromine in mercuric bromide.

A. J. Balard [10] found mercuric bromide is readily soluble in *alcohol*, but not so easily soluble as in *ether*. W. Reinders found this salt to be more soluble than the corresponding iodide; at 0°, alcohol dissolves 13·05 to 13·33 per cent. of mercuric bromide; 16·53 per cent. at 25°; and 22·63 per cent. at 50°; and according to W. Hampe, 9·58 grms. of the salt in 100 c.c. of alcohol at ordinary temp., and 12·62 grms. at the b.p. W. Hampe also measured the electrical conductivity of alcoholic and ethereal soln. W. Herz and G. Anders measured the solubility of mercuric bromide in mixtures of *methyl or ethyl alcohol* and water at 25°, and found the solubility to increase with increasing proportions of alcohol. W. Herz and F. Kuhn measured the solubilities, sp. gr., and viscosities of mercuric bromide in mixtures of methyl and ethyl alcohols; *methyl and propyl alcohols;* and in mixtures of ethyl and propyl alcohols. M. Dukelsky, also, measured the solubility in mixtures of ethyl alcohol and *benzene*. A. J. Balard noted that mercuric bromide is very soluble in ether, and W. Hampe gave the solubility as 0·567 grm. of $HgBr_2$ in a cold soln. of dry ether, and 3·2 grms. in a hot soln. W. Reinders noted that mercuric bromide is more soluble than the iodide in *acetone*—34·58 per cent. at 25°. J. Schröder, H. Steiner, F. Bezold, and A. Naumann found mercuric bromide to be soluble in *methyl acetate*—at 18°, 100 grms. of methyl acetate dissolve 21·93 grms. of mercuric bromide; and 24 grms. of the salt in 100 c.c. of the boiling liquid. A. Naumann and M. Hamers measured the solubility of mercuric bromide in *ethyl acetate*, and found at 18°, 100 grms. of ethyl acetate dissolve 13·05 grms. of mercuric bromide; and W. Herz and G. Anders measured the solubility in mixtures of ethyl acetate and water. W. Reinders found mercuric bromide to be more soluble than the iodide in *diethyl oxalate*. J. H. Mathews found mercuric bromide to be soluble in *allyl mustard oil* and he measured the electrical conductivity of the soln.; A. Werner, in *ethyl sulphide;* L. Mascarelli and M. Ascoli, in *nitrobenzene, nitrotoluene, p-nitroanisole*, and in *α-nitronaphthalene*. O. Sulc found that between 18° and 20° 100 grms. of *chloroform* dissolved 0·126 grm. of mercuric bromide; of *carbon tetrachloride*, 0·003 grm.; of *bromoform*, 0·679 grm.; of *ethyl bromide*, 2·31 grms.; of *ethylene dibromide*, 2·34 grms. C. Mehn noted the solubility of mercuric bromide in *benzene*, and M. S. Sherrill found a litre of benzene dissolved 0·0194 mol of the salt; M. Dukelsky, as indicated above, measured the solubility in mixtures of ethyl alcohol and benzene. M. S. Sherrill also measured the partition coeff. of the salt between water or potassium bromide soln. and benzene free from thiophene. H. N. Morse measured the partition coeff. between *toluene* and water, and between water and $\frac{1}{10}N$-$Hg(NO_3)$, J. Schröder and A. Naumann measured the solubility in *pyridine*. A. Naumann and F. Becker found it is soluble in *benzonitrile*. H. Arctowsky found that, at −10°, *carbon disulphide* dissolves 0·049 per cent. of mercuric bromide; at 0°, 0·087 per cent.; at 10°, 0·122 per cent.; at 20°, 0·187 per cent.; and at 30°, 0·274 per cent.

For the solubility in soln. of the bromides of the alkalies and alkaline earths, *vide infra*. H. N. Morse found a litre of $\frac{1}{10}N$-*mercuric nitrate* dissolves 20 grms. of mercuric bromide. W. A. Isbekoff measured the solubility in soln. of *aluminium bromide*. P. Niggli measured the solubility of mercuric bromide in liquid *sulphur dioxide*, and found at 159·4°, a 1·5 per cent. solubility. W. Herz and W. Paul

found the solubility of mercuric bromide in *bromine water* increased with increasing amounts of bromine, and they found indications of the formation of **mercuric perbromide,** $HgBr_4$.

M. Berthelot[11] exposed moist and also dry purified mercuric bromide to **sunlight** in a sealed tube without noticing any decomposition, and he added that the decomposition which is observed with some pharmaceutical preparations is produced by the **organic matter** which is present. C. Löwig found that aq. soln., when exposed to sunlight, deposited mercurous bromide. W. Reinders observed that some decomposition occurred during the drying of the salt between 70° and 80°, for a specimen became grey, while a sample crystallized from alcohol showed a similar change at 60°. According to M. Kohn and A. Ostersetzer, the mercuric halides are reduced by **hydrogen peroxide** in alkaline soln. or by sodium peroxide, with the precipitation of mercury.

M. Berthelot found that **chlorine** displaced bromine from the dry salt with the evolution of 5·4 Cals., and in soln., 6·0 Cals., while F. Gramp observed no action with iodine with or without water; M. C. Schuyten said that in the presence of an excess of salt, the halogen in mercuric chloride, bromide, or iodide can be replaced by the other halogens except in the action of **iodine** on mercuric bromide, which displaces no bromine. C. F. Rammelsberg noted that **sodium hypochlorite** gave a precipitate of mercuric oxychloride with soln. of mercuric bromide; and, according to A. J. Balard, with **hypochlorous acid,** chlorine and bromine are evolved, and mercuric chloride and bromate are formed.

A. J. Balard said that when mercuric bromide is heated with conc. **sulphuric acid,** bromine is evolved; while H. Rose said this is not the case. G. Viard found the addition of an excess of sulphuric acid to a soln. of the salt, precipitated mercuric bromide. The behaviour of **hydrogen sulphide** on an aq. soln. resembles its action on an aq. soln. of the chloride; with soln. of the bromide in methyl acetate, F. Bezold and A. Naumann obtained a white precipitate of $HgBr_2.2HgS$, which is blackened by light; **ammonium sulphide** in the same soln. gives mercuric sulphide; M. Hamers and A. Naumann also obtained a white precipitate of $HgBr_2$, $2HgS$ with hydrogen sulphide in ethyl acetate soln.; and in pyridine soln., J. Schröder found red mercuric sulphide to be precipitated. According to G. Franceschi, when a few drops of pure alcoholic soln. of hydrogen sulphide are added to an alcoholic soln. of mercuric bromide free from the mercurous salt, a white turbidity is produced, and afterwards mercurous bromide is precipitated—presumably: $2HgBr_2+H_2S=S+2HBr+2HgBr$; if a larger quantity of the hydrogen sulphide soln. is used, but not an excess, a canary-yellow precipitate of $2HgS.HgBr$, *i.e.* $Hg(SHgBr)_2$, is formed, presumably: $H_2S+6HgBr+3S=2HBr+2(HgBr_2.2HgS)$; while if the hydrogen sulphide soln. be in excess, a black precipitate of mercuric sulphide is produced—presumably: $H_2S+2HgS.HgBr_2=3HgS+2HBr$.

A. J. Balard said that when mercuric bromide is heated with **nitric acid,** it gives off the vapour of bromine. The action of ammonia is indicated in a later section. K. A. Hofmann and E. C. Marburg prepared a compound with hydrazine, $(HgBr)_2N_2H_4$, analogous with the corresponding compound with mercuric chloride. They also prepared **mercuric hydrazine bromide,** $HgBr_2.N_2H_4$, also analogous with the chlorine compound. A. Ferratini prepared white prismatic crystals of **hydrazine tribromomercuriate,** $2N_2H_4.HBr.HgBr_2.H_2O$, by mixing soln. of hydrazine hydrobromide and mercuric bromide in mol. proportions, and evaporating in vacuo. The crystals melt at about 73°, and decompose over 150°; they are sparingly soluble in water, and acetic ether; soluble in alcohol and acetone; and insoluble in ether. M. Adams was not able to make a compound with hydroxylamine analogous with $HgCl_2.2NH_2OH$; but he made white quadratic plates of **hydroxylamine tribromomercuriate,** $2NH_2OH.HBr.HgBr_2$. by mixing soln. of the component salts in methyl alcohol. The aq. and alcoholic soln. slowly decompose, forming mercurous bromide; the decomposition is rapid in alkaline soln. C. Löwig found that mercuric bromide and **phosphorus** give phosphorous bromide; and likewise

when heated with **antimony** or **arsenic,** mercuric bromide gives up its bromine to the metal. P. Lemoult observed that **phosphine** is copiously absorbed by soln. of mercuric bromide ; and H. Rose said that a yellow precipitate is formed as in the case of mercuric chloride ; the precipitate becomes black when boiled for a long time with water. H. Arctowsky noted that **calcium carbonate** (marble) gives similar results with soln. of mercuric bromide as with the chloride, and an oxybromide is formed. M. G. Kutscheroff obtained aldehyde by heating mercuric bromide with **acetylene** and water in a sealed tube. T. Harth noted that with two mols of **potassium cyanide** per mol of mercuric bromide, mercuric cyanide and potassium bromide are quantitatively formed, but with two mols of potassium bromide to one of mercuric cyanide no change was observed. H. Grossmann observed that with **potassium thiocyanate** mercuric bromide behaves in an analogous manner to the chloride. C. Löwig noted that a soln. of mercuric bromide is reduced to mercurous bromide when treated with **mercury, copper,** or a soln. of **cuprous bromide** in hydrobromic acid. **Potassium hydroxide** or **sodium hydroxide** was found by W. Sievers to colour mercuric bromide orange-yellow, forming mercuric oxide ; while with a soln. of mercuric bromide, a brownish-black precipitate of a basic salt is formed if the alkali-lye be not in excess, but if it be in excess, mercuric oxide is formed. W. Herz has investigated the equilibrium conditions in this reaction.

As previously indicated, E. Beckmann,[1][2] W. C. Luczizky, and J. S. van Nest have shown that mercuric chloride and bromide probably form a continuous series of mixed crystals ; but since the crystals obtained from a soln. of two salts in alcohol have the crystal-form of neither the chloride nor the bromide—the axial ratios being $a:b:c=0{\cdot}6350:1:1{\cdot}0308$, sp. gr. 5·918, and m.p. 213°—J. S. van Nest suggested that possibly a double salt, **trimercuric tetrabromodichloride,** $HgCl_2.2HgBr_2$, can exist. M. Berthelot gave −6·4 Cals. for the heat of soln. of $HgCl_2+HgBr_2$, and he added that the heat of combination is virtually nil.

H. Edhem-Bey spontaneously evaporated a soln. of mercuric chloroamide, NH_2HgCl, in a very dil. alcoholic soln. of bromine, and obtained plate-like crystals of **mercuric ammonium dibromochloride,** $NH_4Cl.HgBr_2$. J. M. Thomson and W. P. Bloxam examined a sat. soln. of mercuric bromide and ammonium chloride with respect to crystallization when seeded with mercuric bromide or ammonium bromide—the former was active, the latter inactive. They assumed that the soln. contained **trihydrated ammonium mercuric dibromotrichloride,** $HgBr_2.3NH_4Cl.3H_2O$. P. C. Ray obtained **ammonium dimercuric bromotetrachloride,** $NH_4Br.2HgCl_2$, by concentrating soln. of dimercuriammonium bromide, NHg_2Br, in hydrochloric acid. V. Borelli prepared **mercuric perchloratobromide,** $Br.Hg.ClO_4$—*vide* the corresponding iodide—in bundles or in mammillary masses of short white prisms. A soln. of mercuric bromide in one of the perchlorate depresses the f.p., and raises the b.p. It is inferred that mercuric bromide enters these soln. in the form of $HgBr^{\cdot}$-ions, and to a slight extent as $Hg_2Br_2^{\cdot\cdot}$-ions. The presence of complex ions is shown by the variations in the conc. of the mercuric bromide at the electrodes during electrolysis.

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§ 20. Mercuric Oxybromides—Basic Mercuric Bromides

The remarks made about the mercuric oxychlorides apply also to the oxybromides. Many compounds have been reported, but many are probably not chemical individuals. Representing the ratio HgBr : HgO in that order, the compounds 1 : 1, 1 : 2, 1 : 3, 1 : 3½, and 1 : 4 have been reported; and, of these, T. Fischer and H. von Wartenberg [1] believe that only the first two do not exist. In A. J. Balard's method of preparing hypobromous acid by the action of aq. bromine on mercuric oxide, it is often stated that the 1 : 1 oxybromide—**dimercuric oxybromide,** $HgBr_2.HgO$, or Hg_2OBr_2—is formed, but T. Fischer and H. von Wartenberg say that this is only an assumption, and that the product is really an oxybromate, $HgO.Hg(BrO_3)_2$. G. André, however, claimed to have obtained grey crystals of this compound by heating a mixture of the two constituents in the required proportions in a sealed tube to 300°; and he says the heat of the reaction ($HgBr_2$, HgO) is 3·32 Cals. K. Thümmel also reported the formation of red quadratic plates of the 1 : 2 oxybromide—**trimercuric dioxybromide,** $HgBr_2.2HgO$, or $Hg_3O_2Br_2$—by treating undried yellow mercuric oxide with a lukewarm soln. of mercuric bromide; and also by boiling a 1 : 50 soln. of mercuric bromide, 50 parts, with one part of sodium carbonate, and then digesting the product 12 hrs. at 35° to 40°. G. André made it by a process analogous to that used for $HgBr_2.HgO$, and he says that the heat of formation ($HgBr_2$, 2HgO) is 4·4 Cals.

A *citron-yellow* crystalline powder of **tetramercuric trioxybromide,** $HgBr_2.3HgO$, or $Hg_4O_3Br_2$, was prepared by C. Löwig, and by T. Fischer and H. von Wartenberg, by adding insufficient potassium hydroxide to mercuric bromide to precipitate all the mercury, and subsequently boiling the mixture; G. André made it by melting together eq. quantities of the component salts; and K. Thümmel, by treating freshly precipitated mercuric oxide with a lukewarm sat. soln. of mercuric bromide; C. Löwig obtained it in a similar manner. C. F. Rammelsberg made a *dark brown* form of the same salt by precipitation from an aq. soln. of mercuric bromide by the addition of sodium carbonate. T. Fischer and H. von Wartenberg made it by adding to a cold alcoholic soln. of mercuric bromide insufficient alcoholic potash for complete precipitation, and washing the precipitate with alcohol. When heated, K. Thümmel found $HgBr_2.3HgO$ first formed $HgBr_2.4HgO$, then $HgBr_2$ and HgO; and C. Löwig found that at a gentle heat it is resolved into oxygen, a sublimate of mercuric and mercurous bromides, and a residue of mercuric oxide. C. Löwig said that this oxybromide is insoluble in cold water, sparingly soluble in hot water, and soluble in alcohol, but the fact that C. F. Rammelsberg found it to be insoluble in alcohol, makes it probable that C. Löwig's product contained some free mercuric bromide. K. Thümmel says cold alcohol decomposes it, forming mercurous bromide. The reports of the properties of this compound are therefore not concordant.

C. F. Rammelsberg also found the compound is not changed by boiling potash-lye, while C. Löwig says it is wholly converted into mercuric oxide. Ammonia was found by T. Fischer and H. von Wartenberg to convert it into dimercuriammonium oxybromide. C. F. Rammelsberg says that nitric acid dissolves out the mercuric oxide and leaves mercuric bromide as a residue.

T. Fischer and H. von Wartenberg reported the formation of the 1 : 3½ compound—**enneamercuric heptoxybromide,** $2HgBr_2.7HgO$. Brown rhombic plates (yellow in transmitted light) of sp. gr. 9·13, are obtained by heating a mixture of 4·3 grms. of mercuric oxide, 14·4 grms. of mercuric bromide, in 30 c.c. of water for 5 hrs. in a sealed tube at 150°, and afterwards washing the product with hot alcohol; and also by heating a mixture of the two components in a sealed tube at 250°. T. Fischer and H. von Wartenberg also obtained another form of this salt in black rhombic crystals (reddish-brown in transmitted light), and of sp. gr. 8·25, by treating a sat. soln. of mercuric bromide at 60° with a sat. soln. of potassium hydrogen carbonate, and after standing the mixture for two hours, filtering and washing. This compound is decomposed by acids and alkalies, and by potassium bromide, forming mercuric bromide. Ammonia forms dimercuriammonium oxybromide. G. André gives the heat of formation ($HgBr_2$, $3HgO$) as 6·32 Cals.

K. Thümmel obtained the 1 : 4 compound—**pentamercuric tetroxybromide,** $HgBr_2.4HgO$—by heating the 1 : 3 compound either alone or in the presence of water. K. Thümmel, G. André, and T. Fischer and H. von Wartenberg made it by the action of sodium carbonate on a soln. of mercuric bromide; and T. Fischer and H. von Wartenberg made it by the action of potassium hydrogen carbonate on mercuric bromide; by heating a mixture of equimolar proportions of the component salts in the presence of water in a sealed tube at 160°, and subsequently washing out the mercuric bromide with water; by heating in a sealed tube at 200°–300°, a mixture of 8·6 grms. of mercuric oxide and 7·2 grms. of mercuric bromide; by leaving a soln. of mercuric bromide for some weeks in contact with marble or magnesite; and by the action of ozonized air on a slurry of mercurous bromide and water—any mercuric bromide which is formed is removed by alcohol. G. André made it by heating 50 grms. each of red mercuric oxide and mercuric bromide in a litre of water for 12 hrs. to near the b.p. The dark reddish-brown crystalline powder has a sp. gr. 8·73. It is decomposed by heat at 230° into mercuric oxide, and a sublimate of the bromide. Dry ammonia has no action, while aq. ammonia, a soln. of potassium bromide, acids or alkalies act like they do on the 1 : 3½ compound. According to G. André, the heat of formation ($HgBr_2.4HgO$) is 7·8 Cals. The heats of formation of the mercuric oxybromides were found by G. André to be somewhat greater than those of the corresponding oxychlorides.

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§ 21. Compounds of Mercury, Bromine, and Ammonia

Mercuric bromide was found by G. Gore [1] to be moderately soluble in liquid ammonia. According to H. Rose, cold mercuric bromide does not absorb ammonia gas; but when fused at a gentle heat, and cooled in an atm. of the gas, it absorbs 3·41 per cent. approximately eq. to $2HgBr_2.NH_3$. The analyses of the product by H. Rose and E. Mitscherlich are not concordant—presumably on account of the volatilization of some mercuric salt when heated. When the product is treated with water, ammonium bromide passes into soln. and a yellow powder

remains which C. F. Rammelsberg found to give off ammonia gas when treated with potassium sulphide, but not with the hydroxide. According to W. Peters, a mol of mercuric bromide takes up two mols of ammonia when treated in H. Ley and G. Wiegner's apparatus. When aq. soln. of mercuric bromide are treated with aqua ammonia, a white precipitate of the bromamide is obtained: $HgBr_2+2NH_3=NH_4Br+Hg(NH_2)Br$. The product is the bromine analogue of infusible white precipitate, $NH_2Hg.Cl$. J. G. F. Druce said that aq. ammonia reacts with mercurous bromide, forming a mixture of mercury and mercuric bromamide.

Sat. soln. of mercuric bromide in methyl or ethyl acetate give a white precipitate of **mercuric diamminobromide,** $HgBr_2.2NH_3$. A. Naumann and F. Becker used a half-sat. soln. of mercuric chloride in benzonitrile. J. Schröder also examined the action of ammonia on soln. of mercuric bromide in pyridine. R. Widman and L. Pesci also made the diammino-compound by incomplete precipitation from mercuric bromide; and by adding a few drops of ammonia to a soln. of 0·08 grm. of ammonium bromide per c.c. of water sat. with mercuric bromide.

H. Gaudechon made it by pouring a soln. of 50 grms. of mercuric bromide, and 80 grms. of ammonium bromide and 400 c.c. of water, into 100 c.c. of aqua ammonia such that the mol. ratio in the two soln. $NH_3 : HgBr_2$ is greater than 2 : 1. The precipitate was washed by decantation with cold water until it began to show a faint yellow tinge; and it was then allowed to stand in contact with a very dil. soln. of ammonium chloride for some hours until the white colour of the precipitate is restored. The precipitate was then drained, dried on porous tiles, and finally over barium oxide at ordinary temp.

L. Pesci made it by treating dimercuriammonium bromide, NHg_2Br, or the double salt of this compound with ammonium bromide, with a boiling soln. of ammonium bromide; and by the action of alcoholic ammonia on mercuric bromide.

H. Gaudechon found that if a soln. of mercuric bromide at 80° be poured into an excess of ammonia either $HgBr_2.2NH_3$ or NH_2HgBr is formed—all depends on the concentration. He studied mixed soln. of mercuric and ammonium bromides and water in equilibrium with solid phases, and on plotting the conc. of the elements bromine (or nitrogen) and mercury in soln. obtained curves resembling those indicated in Fig. 23. The breaks in the curves corresponded with the solid phases, $HgBr_2.4NHg_2Br$; $Hg(NH_2)Br$; and $HgBr_2.2NH_3$, as shown in the diagram.

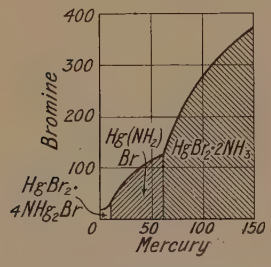


Fig. 23.—Equilibrium of Mercury, Bromine, and Aqueous Ammonia.

According to E. C. Franklin, and F. F. Fitzgerald, a soln. of mercuric bromide in liquid ammonia undergoes amminolysis: $2HgBr_2+4NH_3\rightleftharpoons NHg_2Br+3NH_4Br$; and R. Widman found that with an excess of aqua ammonia on mercuric bromide, the compounds $Hg(NH_2)Br$ and NHg_2Br are formed: $HgBr_2.2NH_3\rightleftharpoons Hg(NH_2)Br+NH_4Br$; and $2Hg(NH_2)Br\rightleftharpoons NHg_2Br+NH_4Br$; followed by $NHg_2Br+2H_2O\rightleftharpoons 2HgO+NH_4Br$. R. Widman also determined the equilibrium conc. of the first two equations, but the extreme slowness of the reaction last symbolized, and the low conc. of the ammonium bromide in soln., prevented the equilibrium conditions being established. It therefore follows that in the presence of an excess of aqua ammonia, mercuric chloride and bromide behave in a similar manner, excepting that with mercuric chloride there is a hydrolysis, forming HgOH—NH—HgCl, whereas with mercuric bromide the hydrolysis occurs in the final stage involved in the formation of mercuric oxide.

Both R. Widman and H. Gaudechon agree that in contact with water alone, mercuric diamminobromide decomposes, forming $Hg(NH_2)Br$ and $HgBr_2.4NHg_2Br$, in accord with the symbols: $HgBr_2.2NH_3\rightleftharpoons Hg(NH_2)Br+NH_4Br$; followed by the amminolysis and diammonation of the basic salt, mercuric bromoamide: $9Hg(NH_2)Br\rightleftharpoons HgBr_2.4NHg_2Br+3NH_4Br+2NH_3$. The further hydrolysis has not been determined, but R. Widman has shown that in the absence of free ammonia,

ammonium bromide soln. acts on mercuric oxide in agreement with the symbols: $9HgO+6NH_4Br \rightleftharpoons 2NH_3+9H_2O+HgBr_2.4NHg_2Br$. In the presence of an excess of mercuric bromide, R. Widman found both $Hg(NH_2)Br$ and $NH(HgBr)_2$ are formed, and he has established the reactions: $HgBr_2.2NH_3 \rightleftharpoons Hg(NH_2)Br+NH_4Br$; followed by $2Hg(NH_2)Br \rightleftharpoons NH(HgBr)_2+NH_3$; and by $2NH(HgBr)_2+3H_2O \rightleftharpoons 3HgO+2NH_4Br+HgBr_2$, and he has further shown that the amminobasic salt $NH(HgBr)_2$ is successively amminolyzed into $Hg_9N_4Br_6$, and then into NHg_2Br, in accord with the equations: $9NH(HgBr)_2+5NH_3=2Hg_9N_4Br_6+6NH_4Br$; followed by $2Hg_9N_4Br_6+4NH_3 \rightleftharpoons 9NHg_2Br+3NH_4Br$.

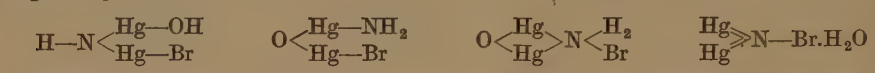
Mercuric diamminobromide is the bromine analogue of fusible white precipitate. L. Pesci, and H. Gaudechon supposed it to be $NHg_2Br.3NH_4Br$, and the latter, on this assumption, gave its heat of formation from the solid compound salts as 9·4 Cals. M. Hamers, and A. Naumann say that mercuric diamminobromide is a white powder without any smell; it melts when heated to 180°, giving off ammonia, and forming a white sublimate. At a higher temp. it forms two volatile substances, one of which forms a pulverulent sublimate and the other condenses as a liquid which solidifies to a crystalline mass. E. Clerici has measured the viscosity constants of the molten liquid. When suspended in water, and treated with hydrogen sulphide, it forms mercuric sulphide and ammonium bromide. It is decomposed by water changing to a yellow colour, and when boiled with water, it breaks down and forms a soln. containing but little mercury, and much ammonia—the reactions involved will appear from what has been said above; similar remarks apply to the action of aqua ammonia, and soln. of mercuric bromide and of ammonium bromide. L. Pesci says that soln. of ammonium chloride, bromide, or iodide slowly dissolve the salt with the evolution of ammonia Alkali-lye decomposes it, forming ammonia and dimercuriammonium bromide, NHg_2Br. It is readily soluble in hydrochloric acid. The soln. in hot dil. sulphuric acid deposits crystals of mercuric bromide on cooling, and it is soluble in acetic acid, but not in alcohol. According to W. Peters, the salt loses ammonia in vacuo. F. Anderlini prepared dark blue crystals of **cupric mercuric tetramminotetrabromide,** $CuHgBr_4.4NH_3$, by mixing a boiling soln. of ammoniacal cupric bromide, and a soln. of mercuric and potassium bromides; and bright blue scales or needles of $CuHg_2Br_6.4NH_3$, by treating a soln. of the preceding compound in a warm soln. of ammonium bromide with mercuric bromide dissolved in potassium bromide in the presence of free ammonia—not in excess.

The bromine analogue of infusible white precipitate was prepared by C. Löwig [2] in 1828, and studied by E. Mitscherlich in 1840. Similar remarks apply to the constitution of both mercuric chloroamide, and bromoamide. According to C. F. Rammelsberg, L. Pesci, H. Gaudechon, and other supporters of the diammonium hypothesis, this compound is assumed to be a double compound of ammonium and dimercuriammonium bromides—namely, $NH_4Br.NHg_2Br$; while, according to R. J. Kane's hypothesis, it is **mercuric bromamide,** $NH_2—Hg—Br$, or possibly, according to E. C. Franklin, $HgBr_2.Hg(NH_2)_2$. C. Löwig, E. Mitscherlich, and L. Pesci made this compound by adding aqua ammonia to a soln. of mercuric bromide. The same compound was found by R. Widman to be a product of the action of mercuric bromide on mercuric diamminobromide.

Mercuric bromoamide is a white powder which is less stable the higher the temp.; according to C. Löwig, it decomposes when heated into nitrogen, ammonia, steam, and a sublimate of mercurous bromide, or, as E. Mitscherlich said, of $HgBr_2.NH_3$; the residue is $HgBr_2.2NHg_2Br$. E. Mitscherlich also says that this compound is insoluble in water and alcohol. L. Pesci noted an indefinitely large proportion of ammonium bromide could be extracted by washing with water; and that boiling water produces a yellow product which approximates closer and closer to NHg_2Br. H. Gaudechon says that water decomposes it, forming $HgBr_2.4NHg_2Br$; the reaction at 15° is represented by $9Hg(NH_2)Br=HgBr_2.4NHg_2Br+2NH_3+3NH_4Br$; and at 100°, $10Hg(NH_2)Br=HgBr_2.4NHg_2Br+2NH_4Br+4NH_3+HgBr_2$. E. Mitscherlich found it to be slightly soluble in aqua ammonia; and

H. Gaudechon noted that after standing at 8° to 10° in contact with ammonium bromide the solid phase is $HgBr_2.2NH_3$. H. Gaudechon and R. Widman have studied the equilibrium conditions. H. Saha and K. N. Choudhuri obtained **dihydrated mercuric oxybromoamide,** $HgO.Hg(NH_2)Br.2H_2O$, by shaking aqua ammonia of sp. gr. 0·895 with mercurous bromide, and evaporating the ammoniacal filtrate in vacuo over sulphuric acid; the resulting white powder was washed with water and dried over calcium chloride. When heated, ammonia is evolved and a black mass remains, and at a higher temp. a sublimate of mercurous bromide and mercury is formed. Boiling potash-lye colours it yellow.

Mercuric hydroxybromoamide, HgOH.NH.HgBr.—This compound can be regarded as the bromide of Millon's base, it can also be regarded as *oxydimercuriammonium bromide,* OHg_2NH_2Br, or as *hydrated dimercuriammonium bromide.* Graphically:



It is formed, according to P. C. Ray, when the salt $NH_4Br.4HBr$ is treated with an excess of potassium hydroxide. K. A. Hofmann and E. C. Marburg made it by digesting Millon's base in darkness for 24 hrs. with a 3 per cent. soln. of hydrobromic acid, washing the product with the same acid, then with alcohol and ether, and drying 24 hrs. in vacuo over sulphuric acid. Attempts to dehydrate the product have been nugatory; it decomposes at 200°. K. A. Hofmann and E. C. Marburg also prepared what they regarded as *dihydrated dimercuriammonium bromide,* $NHg_2Br.2H_2O$, but what E. C. Franklin regarded as **hydrated mercuric hydroxybromoamide,** $HgOH.NH.HgBr.H_2O$. The alternative formula, $(HgOH)_2NH_2Br$, has also been suggested. This compound is formed as a yellow powder by treating an aq. soln. of mercuric bromide with dil. aqua ammonia, and washing the product with dil. ammonia, then with alcohol and ether, and finally drying in vacuo.

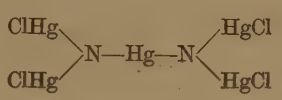
L. Pesci prepared what he regarded as a double salt, $4NHg_2Br.5NH_4Br$, but which E. C. Franklin regarded as **mercuric diammino-enneabromoamide,** $7Hg(NH_2)Br.HgBr_2.2NH_3$, by the action of ammonium carbonate on an aq. soln. of mercuric bromide; by passing carbon dioxide through a strongly ammoniacal soln. of mercuric bromide; or by allowing the soln. to stand exposed to the air. The product is washed with a dil. soln. of ammonium carbonate, and dried over sulphuric acid. It forms minute needle-like crystals, which, when heated, decompose without melting, forming ammonia, etc. The compound is decomposed by water, forming ammonium bromide and mercuric bromoamide. Hot alkali-lye transforms it into dimercuriammonium bromide, NHg_2Br, with the evolution of ammonia. It is easily soluble in hydrochloric acid; insoluble in conc. nitric acid; and it is soluble in a warm 10 per cent. soln. of sulphuric acid—and on cooling, the last-named soln. deposits crystals of mercuric bromide. It dissolves slowly in soln. of ammonium chloride, bromide, or iodide with the evolution of ammonia. The constitution and therefore also the name of this product is not clear; nor is it known if a true compound or mixed crystals of two or more compounds are in question.

R. Widman prepared **mercuric dibromoamide,** $NH(HgBr)_2$, by treating mercuric bromoamide, $Hg(NH_2)Br$, with a soln. of mercuric bromide: $3Hg(NH_2)Br + HgBr_2 \rightleftharpoons 2NH(HgBr)_2 + NH_4Br$—*vide supra*—and also by shaking mercuric oxide with a soln. of mercuric and ammonium bromides. The white powder is rapidly blackened by exposure to diffuse daylight; it is decomposed by water; a dil. ammoniacal soln. of ammonium bromide converts it back into mercuric bromoamide.

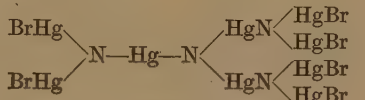
Mercuric tetrabromoamide, $(HgBr)_2N.Hg.N(HgBr)_2$, is also regarded by E. C. Franklin as possibly having the composition $2HgBr_2.Hg_3N_2$; and by H. Gaudechon as having the composition $2NHg_2Br.HgBr_2$, which he calls *dimercuriammonium dibromomercuriate;* and he gives the heat of formation from the solid component salts as 10·9 Cals. H. Gaudechon made it by treating a more or less conc. soln. of mercuric bromide at 80° with sufficient ammonia for the mol. ratio $HgBr_2 : NH_3$ not to exceed 1 : 18. P. C. Ray made it by gradually adding potash-lye—not in excess—to a boiling soln. of ammonium pentabromomercuriate,

$NH_4Br.2HgBr_2$. When the yellow powder is digested with water, it gives up so little mercury, bromine, and nitrogen to the solvent that H. Gaudechon could not decide whether the soluble matter was due to decomposition or soln. It is decomposed by hot water into dimercuriammonium bromide, NHg_2Br, and *dimercuriammonium hexabromomercuriate*, $HgBr_2.4NHg_2Br$.

H. Gaudechon explains the formation of the compounds $HgCl_2.2NHg_2Cl$, and of $HgBr_2.2NHg_2Br$, on the assumption that the halogen salts of dimercuriammonium when given the choice of water, or ammonium or mercuric halide, unite by preference with the mercuric halide to form what he calls in the case of $HgCl_2.2NHg_2Cl$, *chloromercurate de dimercuriammonium*, and in the case of $HgBr_2.4NHg_2Br$, *bromomercurate de dimercuriammonium*. E. C. Franklin regards these compounds as amminobasic salts or mixtures formed in the presence of insufficient ammonia to give basic compounds richer in nitrogen ; and he shows that the structural formulation applied to ordinary basic salts is also applicable :



$HgCl_2.2NHg_2Cl$



$HgBr_2.4NHg_2Br$, or $Hg_5N_4Br_6$

H. Gaudechon made the compound $HgBr_2.4NHg_2Br$, or $(HgBr)_2N.Hg.N : [Hg.N(HgBr)_2]_2$, by pouring a litre of an aq. soln. of mercuric bromide sat. at 15° into a litre of aqua ammonia so that the mol. ratio $HgBr_2 : NH_3$ is rather more than 1 : 2. Next day the liquid was decanted from the orange-yellow precipitate, and the precipitate washed free from bromine and ammonia by cold or lukewarm water, and dried on porous tiles at 15°, and then in darkness at 100°. H. Gaudechon also obtained this same product by using an ammoniacal soln. of ammonium bromide with the soln. of mercuric bromide ; and by washing $Hg(NH_2)Br$ or $HgBr_2.2NH_3$ with hot or cold water until the washings are free from bromine or ammonia. R. Widman studied the conditions of equilibrium of this salt with soln. of ammonia and ammonium bromide—*vide supra*—with aqua ammonia it forms mercuric bromoamide, $2N_4Hg_9Br_6+4NH_3=9NHg_2Br+3NH_4Br$. According to H. Gaudechon, the heat of formation of $HgBr_2.4NHg_2Br$, from the solid component salts is 15·2 Cals.

Dimercuriammonium bromide, or *tetramercuriammonium bromide*, NHg_2Br.—This product may be regarded as a basic mixture, $HgBr_2.Hg_3N_2$. L. Pesci made it by treating dimercuriammonium enneabromomercuriate, $5NH_4Br.4NHg_2Br$, or $HgBr_2.7Hg(NH_2)Br.2NH_3$, with warm alkali-lye, or by treating Millon's base with dil. hydrobromic acid, and, in either case, drying the product in vacuo over sulphuric acid. H. Gaudechon made it by treating two mols of dimercuriammonium hexabromomercuriate, $HgBr_2.4NHg_2Br$, with four mols of ammonia in a hot conc. soln., and drying the product at 100°, or else at 15° over barium oxide. H. Gaudechon also made it by treating dimercuriammonium oxide, $(NHg_2)_2O.2H_2O$, with hydrobromic acid for 24 hrs. in darkness, drying the product on porous tiles, and finally at 15° over barium oxide, and then at 100°. E. C. Franklin made it by adding a soln. of potassium amide to an excess of a soln. of mercuric bromide in liquid ammonia, and thoroughly shaking the mixture. F. F. Fitzgerald made it by thoroughly mixing an aq. soln. of potassium amide with an excess of a similar soln. of mercuric bromide, and after standing 24 hrs., washing the precipitate. R. Widman said that this compound is precipitated from ammoniacal soln. of mercuric bromide, when the conc. of ammonium bromide is less than 0·0008 grm. per c.c. If a hot soln. of mercuric bromide is poured into a cold aq. soln. of ammonia, a white or yellow precipitate is formed, which, when washed with water, furnishes **monohydrated dimercuriammonium bromide,** $NHg_2Br.H_2O$. If the soln. be mixed in the converse way, and the precipitate be washed, a deep yellow precipitate of dimercuriammonium hexabromomercuriate is formed. If the latter

be well washed with hot conc. ammonia, a canary-yellow dimercuriammonium bromide is formed. This does not combine with water to form the monohydrate, nor is the anhydrous salt formed by heating the monohydrate.

Dimercuriammonium bromide is a canary-yellow powder, which H. Gaudechon found to consist of very small crystals. According to this *savant*, the heat of formation of this compound from its elements is —17·6 Cals. L. Pesci said that when heated, it decomposes without melting, giving off ammonia ; and H. Gaudechon said that it explodes if rapidly heated to redness, but if gradually heated to 400°, blue sparks appear in the mass and mercury and mercurous bromide are formed. This salt is insoluble in water, and it is not hydrated after standing 15 days in water or in an atm. sat. with water vapour ; L. Pesci said that it is insoluble in conc. nitric or sulphuric acid, and F. F. Fitzgerald obtained only a small residue—probably mercurous bromide, when the salt is boiled for a long time with sulphuric acid ; it is readily soluble in hydrochloric acid. E. C. Franklin found it to be soluble in aq. soln. of acid, and ammoniacal salts ; and L. Pesci found it to dissolve slowly in soln. of ammonium chloride, bromide, or iodide with the evolution of ammonia. R. Widman, and H. Gaudechon have studied the conditions of equilibrium of this compound with water and ammoniacal salts—*vide supra*. E. C. Franklin found it to be converted into mercuric nitride, Hg_3N_2, by potassium amide.

What P. C. Ray regarded as *hemihydrated dimercuriammonium bromide*, $2NHg_2Br.H_2O$, and E. C. Franklin as **dimercuriammonium hydroxybromoamide,** $NHg_2Br.HgOH.NH.HgBr$, was made as a deep red precipitate by P. C. Ray, and J. Sen, by treating $NH_4Br.2HgBr_2$ with an excess of dil. potassium hydroxide, and drying at 100°. This product is decomposed by heat into nitrogen, mercury, water, and mercurous bromide. The salt, $NHg_2Br.H_2O$, is considered to be $HgOH.NH.HgBr$; and $NHg_2Br.2H_2O$, to be $HgOH.NH.HgBr.H_2O$.

H. Gaudechon made **dimercuriammonium hemiamminobromide,** $2NHg_2Br.NH_3$, by exposing dimercuriammonium bromide to the action of ammonia under press. When the contents of the tube have changed to a red colour, the tube is cooled so as to liquefy the ammonia. The tube is then opened, and the excess of liquid ammonia poured off. The product is then allowed to stand in a bath of methyl chloride at —21° until no more gas is developed. The red product can be kept at 4°–5° without much change, but in 15 hrs. at 15°, it loses about one-third of its ammonia, and if kept over phosphorus pentoxide, it loses one-fourth of its ammonia, forming hydrated dimercuriammonium amminobromide, $4NHg_2Br.NH_3.H_2O$, as a hygroscopic powder :

The compound *dimercuriammonium hydrobromide*, $NHg_2Br.4HBr$, is considered to be ammonium pentabromomercuriate, $2HgBr_2.NH_4Br$; the compound $NHg_2Br.HBr$ is supposed to be $NH(HgBr)_2$, the dibromide of Millon's base, or mercuric dibromoamide ; the compound $NHg_2Br.NH_4Br$ is better regarded as mercuric bromoamide, $Hg(NH_2)Br$; the compound $4NHg_2Br.5NH_4Br$ is also considered to be mercuric diammino-enneabromoamide, $7Hg(NH_2)Br.HgBr_2.2NH_3$; and the compound $NHg_2Br.3NH_4Br$ may be regarded as mercuric diamminobromide, $HgBr_2.2NH_3$.

According to M. Adams,[3] hydroxylamine does not unite with mercuric bromide to form stable salts of the type $MBr_2(NH_2OH)_2$. An alcoholic soln. of normal hydroxylamine hydrobromide, cooled below zero, dissolves mercuric oxide, but the cold soln., on standing, furnishes white crystals of dihydroxylamine hydrobromide : $HgO+4(NH_4OH.HBr)=HgBr_2+2(NH_2OH)_2HBr+H_2O$. If mol. proportions of the two salts, in methyl alcohol soln., cooled below zero, be treated with a methyl alcohol soln. of hydroxylamine, and ether added, microscopic quadratic plates of **mercuric tetrahydroxylamine dihydrobromide,** $HgBr_2(NH_2OH)_2(NH_2OH.HBr)_2$, are formed. The crystals are soluble in methyl alcohol, forming a soln. which decomposes slowly ; the aq. soln. decomposes rapidly. The salt is less stable than the corresponding chloride. The methods used for the preparation of mercuric dihydroxylamine chloride fail when employed in the attempt to make the corresponding bromide.

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§ 22. Double and Complex Salts of Mercuric Bromide—The Bromomercuriates

According to R. Varet,[1] the double bromides are derivatives of the complex acids $HHgBr_4$ and $H_2Hg_2Br_6$. C. Löwig noted that hydrobromic acid of sp. gr. 1·18 when sat. at 40° with mercuric bromide, forms a syrupy liquid in which the two components are in the proportions $HBr.HgBr_2$, that is, **hydrotribromomercuric acid,** $HHgBr_3$; and G. Neumann adds that this compound exists only at temp. exceeding 4°. R. Varet gives the heat of formation $HBr+HgBr_2=2·54$ Cals. and $2HBr+HgBr_2=2·30$ Cals. at 17°, and M. Berthelot gives $HgBr_2$ (one eq. in 40 litres)+2HBr (one eq. in two litres)=3·4 Cals. at 11°, and with 4HBr, under similar conditions, 5·4 Cals. with crystalline $HgBr_2$-4HBr in a soln. of similar concentrations, 3·0 Cals., and with 12HBr, 2·0 Cals. The properties of the product resemble those of the corresponding hydrotrichloromercuric acid. C. R. Crymble also noted the resemblance between the complexes $HHgCl_3$ and $HHgBr_3$. If the soln. of hydrotribromomercuric acid be cooled or diluted with water, half the mercuric bromide is precipitated and the compound $2HBr.HgBr_2$, that is, **dihydrotetrabromomercuric acid,** H_2HgBr_4, remains in soln., and G. Neumann added that this product is formed in soln. at 11°. C. Löwig noted that mercuric bromide is readily soluble in soln. of ammonium bromide, and that the addition of alkali carbonates precipitates mercuric bromoamide, $Hg(NH_2)Br$.

P. C. Ray prepared crystals of **ammonium pentabromomercuriate,** $2HgBr_2.NH_4Br$, or $NH_4Hg_2Br_5$, by the action of hydrobromic acid on dimercuriammonium nitrite. The soln. is then evaporated; the same salt is made by evaporating a soln. of the component salts in the presence of hydrobromic acid. The white prismatic and tabular crystals probably belong to the triclinic system; they are decomposed by water into their components; alkali hydroxides form $NHg_2Br.\frac{1}{2}H_2O$, *i.e.* $NHg_2Br.HgOH.NH.HgBr$; and also $2NHg_2Br.HgBr_2$, *i.e.* $(HgBr)_2N.Hg.N(HgBr)_2$. E. Clerici has measured the viscosity constants. R. Varet gives the heat of formation 2·22 Cals. by mixing soln. of the component salts; R. Varet also gave 2·63 Cals. for the hypothetical $HgBr_2.NH_4Br$. An alternative formulation for $2HgBr_2.NH_4Br$ is $NHg_2Br.4HBr$.

R. Varet[2] deduced the formation of **lithium tribromomercuriate,** $HgBr_2.LiBr$, with a heat of formation of 1·35 Cals., and of **lithium tetrabromomercuriate,** $HgBr_2.2LiBr$, with a heat of formation of 2·50 Cals., by mixing aq. soln. of the

component salts. F. Calzolari and U. Tagliavini prepared **lithium mercuric bromodichloride,** or *lithium bromodichloromercuriate,* $HgCl_2.LiBr$, but could not get it in the crystalline form ; although the complex with hexamethylenetetramine readily crystallized. P. A. von Bonsdorff prepared deliquescent needles and rhombic prisms of sodium bromomercuriate ; and T. Harth also prepared this salt. E. Clerici determined the viscosity constants. R. Varet gave the heat of formation of **sodium tribromomercuriate,** $HgBr_2.NaBr$, as 1·28 Cals. at 17°, and of **sodium tetrabromomercuriate,** $HgBr_2.2NaBr$, as 2·30 Cals. A. Vicario preferred the last-named salt to mercuric bromide for hypodermic injections ; the soln. is quite neutral and does not coagulate albumen. A. Vicario also prepared **sodium dichlorodibromomercuriate,** $HgBr_2.2NaCl$, from soln. of the component salts.

According to C. Löwig, a conc. aq. soln. of two mols of potassium bromide dissolves more than three mols of mercuric bromide, forming a stiff opaque mass which when cooled or diluted with water, deposits mercuric bromide until two mols remain in soln. W. Herz and W. Paul measured the solubility of mercuric bromide in soln. of potassium bromide at 25°. Expressing the results in milligram-mols per 10 c.c. :

KBr . .	0	2·19	7·70	23·80	34·70
$HgBr_2$ . .	0·17	0·98	4·72	13·60	19·30

When the soln. of equimolar parts of the two salts is evaporated, P. A. von Bonsdorff obtained prismatic crystals of what is thought to be **potassium tetrabromomercuriate,** $HgBr_2.2KBr$, or K_2HgBr_4. These crystals are stable in air. According to J. Thomsen, the heat of formation (Hg, Br_2, 2KBr, aq.)=52·19 Cals., ($HgBr_2$, 2KBr)=1·23 Cals. ; ($HgBr_2$, 2KBr, aq.)=1·64 Cals. ; and for solid K_2HgBr_4, 242·4 Cals. The heat of soln. of a mol of K_2HgBr_4 in 600 mols of water is −9·75 Cals. M. Berthelot gives the heat of formation in soln. at 8°, as ($HgBr_2.2KBr$), 5·0 Cals., and for $HgBr_{2aq.}+4KBr_{aq.}$=8·2 Cals., and of $HgBr_{2aq.}+8KBr$=9·6 Cals., so that higher double salts than the 1 : 2 compound are supposed to be formed. R. Varet gives for the heat of formation $HgBr_2.2KBr$, 2·36 Cals. S. Bugarszky represents the equilibrium conditions between a soln. of potassium bromide and yellow mercuric oxide by $4KBr+HgO+H_2O \rightleftharpoons 2KOH+K_2HgBr_4$. R. G. van Name and W. G. Brown studied the equilibrium conditions in soln. of mercuric and potassium bromides, and obtained evidence of the formation of the double salt, $2KBr.HgBr_2$. Yellow octahedral crystals of **potassium tribromomercuriate,** $HgBr_2.KBr$, or $KHgBr_3$, were prepared by C. Löwig by evaporating a moderately conc. soln. of potassium bromide sat. with mercuric bromide. F. W. Clarke gave the sp. gr. as 4·412 (17·2°), 4·419 (24·5°), and 4·3996 (20·5°). According to M. Berthelot, the heat of formation for the crystalline double salt is 3·1 Cals., for the soln. at 8°, 2·75 Cals., and for the heat of soln., −8·9 Cals. The crystals melt when heated, and at a higher temp. furnish a sublimate of mercuric bromide and a residue of potassium bromide. Water precipitates half the combined potassium bromide. P. A. von Bonsdorff prepared crystals of **hydrated potassium tribromomercuriate,** $HgBr_2.KBr.H_2O$, or $KHgBr_3.H_2O$, which F. W. Clarke found to have a sp. gr. 3·865 (20°–24°), and M. Berthelot, a heat of formation of 6·4 Cals., and a heat of soln. of −2·2 Cals. T. Harth prepared long needle-like crystals of **potassium dibromodichloromercuriate,** $HgBr_2.2KCl$, by crystallization from a mixed soln. of mercuric bromide and potassium chloride or potassium bromide and mercuric chloride in eq. proportions. T. Harth found the salt to be soluble in water, and at the same time to be decomposed with the separation of mercuric bromide if insufficient water is present to dissolve the latter. Ether also extracts mercuric bromide from the aq. soln. The electrical conductivity of the aq. soln. has also been measured.

H. L. Wells has prepared a series of cæsium bromomercuriates, and chlorobromomercuriates, and S. L. Penfield has measured the crystallographic constants. The ratio $HgBr_2$: CsBr is 1 : 3, 1 : 2, 1 : 1, and 2 : 1. All the salts are white excepting

the 1 : 1 salt, which has a lemon-yellow colour in spite of the fact that the constituents are both white. All the salts when recrystallized one or more times from water, yield the 2 : 1 salt, **cæsium pentabromodimercuriate,** $CsHg_2Br_5$, or $2HgBr_2.CsBr$, with the chlorides, the 1 : 1 salt is the stable form with water. If alcohol be used for the recrystallization of the double bromide, then the 1 : 1 salt is the stable form. The crystals of the 2 : 1 salt are rhombic pseudohexagonal plates with axial ratios $a : b : c = 0{\cdot}590 : 1 : 1{\cdot}15$. The solubility in water is 0·807 per cent. at 16°; the salt is sparingly soluble in hot alcohol and furnishes what are probably monoclinic crystals of $CsHgBr_3$; under similar conditions, the cubic form of $CsHgCl_3$ crystallizes from alcoholic soln. Cubic crystals of the 1 : 1 salt, **cæsium tribromomercuriate,** $CsHgBr_3$, are formed as in the analogous case of the chloro-salt, when an excess of the cæsium halides is present, and a dimorphous variety in monoclinic crystals with axial ratios $a : b : c = 1{\cdot}0124 : 1 : 0{\cdot}70715$, and $\beta = 87° 7'$ is deposited when the halide is not present in the soln. in so great an excess. Unlike the corresponding chloride, the second form of this salt is decomposed by crystallization from water and the 2 : 1 salt is formed, but if the latter be recrystallized from alcohol the monoclinic form of the 1 : 1 salt is obtained. The general appearance and mode of preparation of the 1 : 2 salt, **cæsium tetrabromomercuriate,** Cs_2HgBr_4, or $2CsBr.HgBr_2$, is exactly like the corresponding chloride. The rhombic bipyramidal crystals have the axial ratios $a : b : c = 0{\cdot}5706 : 1 : 1{\cdot}4715$; and, according to E. von Fedoroff, they are isotectoric with those of potassium sulphate, K_2SO_4, potassium tetrafluoberylliate, K_2BeF_4, and potassium tetrachlorozincate, K_2ZnCl_4. The 1 : 3 salt, **cæsium pentabromomercuriate,** Cs_3HgBr_5, or $HgBr_2.3CsBr$, is prepared exactly like the corresponding chloride and the slender prismatic crystals belong to the rhombic system, and have the axial ratios $a : b : c = 0{\cdot}7966 : 1 : 0{\cdot}6656$. They are isomorphous with the corresponding chloride.

H. L. Wells also prepared double compounds of cæsium chloride and mercuric bromide; and although the two salts unite together quite readily, there is a general tendency to form unmixed salts—all the chlorobromides finally yield mercuric bromide when recrystallized from water. All the chlorobromides are colourless excepting the pale yellow $CsHgClBr_2$. The representative of the 1 : 3 type, **cæsium trichlorodibromomercuriate,** $Cs_3HgCl_3Br_2$, or $HgBr_2.3CsCl$, is obtained from mixed soln. with a large excess of cæsium chloride. It forms slender prisms with axial ratios $a : b : c = 0{\cdot}7882 : 1 : 0{\cdot}6527$. The representative of the 1 : 2 type, **cæsium dichlorodibromomercuriate,** $CsHgBr_2Cl_2$, or $HgBr_2.2CsCl$, is also formed when a large excess of cæsium chloride is present. The thin rectangular plates are rhombic bipyramids with axial ratios $a : b : c = 0{\cdot}567 : 1 : —$. The representative of the 1 : 1 salt, **cæsium chlorodibromomercuriate,** $CsHgClBr_2$, or $HgBr_2.CsCl$, forms pale yellow dimorphous crystals—cubic and rhombic with axial ratios approximately the same as the corresponding chloro-salt. It is possible that mixed crystals of the 1 : 1 chloro- and bromo-salts are in question. The 2 : 1 salt, cæsium chlorotetrabromodimercuriate, $2HgBr_2.CsCl$, or $CsHg_2ClBr_4$, forms rectangular plates belonging to the rhombic system with axial ratios $a : b : c = 0{\cdot}586 : 1 : —$. When this salt is recrystallized from water, it furnishes crystals of **cæsium chlorodecabromopentamercuriate,** $CsHg_5ClBr_{10}$, $5HgBr_2.CsCl$, belonging to the monoclinic system with axial ratios $a : b : c = 0{\cdot}7111 : 1 : 0{\cdot}4561$, and $\beta = 85° 29'$. These crystals are strongly double refracting.

A. Mailhe obtained a green **cupric mercuric oxybromide,** $CuO.HgBr_2.3H_2O$, by the action of a soln. of cupric bromide on mercuric oxide; and also a blue powder, $3CuO.CuBr_2.2HgBr_2.H_2O$, by the action of a soln. of cupric bromide on yellow mercuric oxide. A. Werner represented the latter by the formula:

$$Cu\left[\begin{matrix}HO\\HO\end{matrix}Cu\right]_3Br_2.2HgBr_2.H_2O$$

W. Herz and W. Paul measured the solubility of mercuric bromide in soln. of calcium bromide and found the solubility increased *pari passu* with increasing

proportions of calcium bromide. At 25°, expressing conc. in milligram-mols in 10 c.c. of soln. :

$CaBr_2$.	0	0·72	6·45	18·92	24·79	37·54
$HgBr_2$.	0·17	1·17	6·76	13·58	27·66	36·66

P. A. von Bonsdorff found that when an aq. soln. of calcium bromide is sat. with mercuric bromide, and then evaporated, it (i) yields lustrous octahedral and tetrahedral crystals which are permanent in air, and decompose when treated with a small proportion of water. The crystals dissolve completely on the application of heat, and crystallize out again on cooling. (ii) When the mother liquid remaining after the separation of the first crop of crystals is further evaporated, it yields prismatic or acicular crystals which deliquesce rapidly even in dry air, and which contain a smaller proportion of mercuric bromide than the preceding salt. R. Varet found the heat formation of **calcium tetrabromomercuriate,** $CaHgBr_4$, to be 2·82 Cals., and of **calcium hexabromodimercuriate,** $2HgBr_2.CaBr_2$, or $CaHg_2Br_6$, 3·10 Cals., when the component salts are mixed in aq. soln. at 17°. C. Löwig prepared **strontium hexabromodimercuriate,** $SrHg_2Br_6$, or $2HgBr_2.SrBr_2$, by dissolving three mols of mercuric bromide in a soln. of a mol of strontium bromide in twice its weight of water at 50°. When the soln. cools, it deposits a mol of mercuric bromide, and the mother liquid, when evaporated, yields crystals of the salt in question. When digested with water, C. Löwig found the mercuric bromide remains undissolved, and the liquid furnishes crystals of **strontium tetrabromomercuriate,** $SrHgBr_4$, or $HgBr_2.SrBr_2$, on evaporation. R. Varet found the heat of formation of $2HgBr_2.SrBr_2$ from soln. of the component salts at 17° to be 3·06 Cals., and of $HgBr_2.SrBr_2$, 2·68 Cals. The 1 : 1 salt is soluble in all proportions of water. W. Herz and W. Paul measured the solubility of mercuric bromide in soln. of strontium and of barium bromides. P. A. von Bonsdorff prepared lustrous prismatic crystals of barium bromomercuriate. R. Varet gives the heat of formation of **barium hexabromodimercuriate,** $2HgBr_2.BaBr_2$, or $BaHg_2Br_6$, prepared by mixing soln. of the component salts at 17°, as 3·17 Cals., and for **barium tetrabromomercuriate,** $HgBr_2.BaBr_2$, or $BaHgBr_4$, 2·91 Cals.

P. A. von Bonsdorff evaporated a mixed soln. of magnesium and mercuric bromides over sulphuric acid, and the first crop of crystals which separate as broad plates were thought to be **magnesium hexabromodimercuriate,** $MgHg_2Br_6$, or $2HgBr_2.MgBr_2$; and the second crop of deliquescent crystals, **magnesium tetrabromomercuriate,** $MgHgBr_4$, or $HgBr_2.MgBr_2$. F. Calzolari and U. Tagliavini prepared crystals of a complex of $MgBr_2.2HgBr.10H_2O$ with hexamethylenetetramine. R. Varet gives 3·07 Cals. for the heat of formation of the former by mixing soln. of the component salts at 17° ; and 2·8 Cals. for the latter. W. Herz and W. Paul have measured the solubility of mercuric bromide in soln. of magnesium bromide at 25°. P. A. von Bonsdorff also prepared prisms and plates of the double bromide of zinc and mercury which are permanent in dry air, and deliquescent in moist air—they are probably $ZnHgBr_4$. By mixing soln. of the component salts at 17°, R. Varet found the heat of formation of **zinc hexabromodimercuriate,** $2HgBr_2.ZnBr_2$, or $ZnHg_2Br_6$, to be 2·82 Cals., and of **zinc tetrabromomercuriate,** $HgBr_2.ZnBr_2$, or $ZnHgBr_4$, 2·56 Cals. A. Mailhe prepared white monoclinic prisms and hexagonal plates of **zinc oxybromomercuriate,** $ZnO.HgBr_2.8H_2O$, by digesting mercuric oxide with a soln. of zinc bromide. Prismatic needles of the corresponding **cadmium oxybromomercuriate,** $CdO.HgBr_2.8H_2O$, were also prepared. R. Varet gives 2·2 Cals. for the heat of formation of **cadmium hexabromodimercuriate,** $2HgBr_2.CdBr_2$, or $CdHg_2Br_6$, by mixing aq. soln. of the component salts at 17° ; and for **cadmium tetrabromomercuriate,** $HgBr_2.CdBr_2$, or $CdHgBr_4$, 2·44 Cals. C. Sandonnini studied the f.p. curve of mixtures of mercuric and lead bromides. There is a eutectic at 232°, with five mols per cent. of lead bromide, but there is no sign of the formation of *lead bromomercuriates.*

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§ 23. Mercurous Iodide

Mercury forms two iodides—mercurous iodide, HgI; and mercuric iodide, HgI_2. The two elements unite together at ordinary temp., and, according to W. A. Shenstone,[1] the reaction occurs only if moisture be rigorously excluded. A mixture of the two iodides is formed by triturating the two elements together, and A. R. von Schrötter noted that if mercury be placed in a dish, and iodine or a sat. soln. of iodine in potassium iodide be placed in another dish, and both be confined under a jar, the mercury becomes dark violet and finally changes to red mercuric iodide. According to C. Brame, if mercury and iodine are placed in different parts of a tube, the mercury iodide is formed at a distance away from both elements, showing that combination probably takes place between their vapours. According to H. Gautier and G. Charpy, the reaction between mercury and an aq. or alcoholic soln. of iodine is fairly rapid. According to M. Berthelot, hydrogen iodide reacts fairly quickly with mercury, and G. H. Bailey and G. J. Fowler noted the reaction occurs in the absence of oxygen. Green mercurous iodide is first formed very rapidly, and this is converted by an excess of hydrogen iodide into red mercuric iodide. The mercuric iodide is reconverted to mercurous iodide if an excess of mercury be added. Mercury is decomposed by aq. hydriodic acid more readily than by hydrobromic acid.

The preparation of mercurous iodide.—(1) *From mercury and iodine.*—Mercurous iodide was made by J. B. Berthemot [2] by triturating equi-grammolar proportions of the two elements—preferably moistened with alcohol. The iodine is dissolved by the alcohol and quickly transferred to the mercury. According to E. Siller, much heat is evolved during the trituration, the mass liquefies, and iodine vapour is given off. On cooling, a reddish-brown mass is produced; if this be ground with alcohol, a greenish-yellow powder is obtained. The product is always contaminated with a little mercuric iodide; and L. Mailhe showed that even if a less than an equi-molar proportion of iodine be employed, some mercuric iodide is produced during the action. The mercuric iodide can be removed by leaching the product with alcohol, and E. Soubeiran recommended washing out the mercuric iodide with boiling alcohol. He found that some mercuric iodide is extracted even when the mercury has been rubbed up with but half its weight of iodine. The product must then contain some free mercury. F. R. Williams recommended extracting the mercuric iodide with a soln. of sodium chloride; and M. François, with cold ether. E. Riegel failed to obtain products of a constant composition by the trituration process. When mercury is agitated with a soln. of iodine, mercurous iodide is formed, but if other metals be present the iodide of that metal may be formed

before the mercury is attacked. Thus, H. Gautier and G. Charpy found this to be the case when lead amalgam is shaken up with a brown soln. of iodine in alcohol, ether, or acetone. Yellow lead iodide is first formed and the mass then becomes green owing to the formation of mercurous iodide; they also say that violet soln. of iodine in carbon disulphide or chloroform gives green mercurous iodide just as would be the case if lead were absent. They explain the action by assuming that the mercuric iodide first formed is transformed by the lead into mercurous iodide, and mercuric iodide is regenerated by the excess of iodine. According to E. Beckmann and A. Stock, the action rests on the difference in the solubility of the mercuric iodide—in alcoholic soln. the mercuric iodide is reduced by lead, but it is precipitated by chloroform as finely divided mercury and mercurous iodide which reacts with difficulty with the lead. If water be used instead of alcohol for the trituration the mercury and iodine combine more slowly, but the reaction is quicker if the mixture be heated; the product of the trituration with water is brownish-red, and with alcohol yellowish-green. M. François treated mercury with a soln. of iodine in *N*-KI, saturated at 20°, forming mercurous iodide until the soln. has 11·9 grms. of mercuric iodide per 100 c.c. at 20°. Nessler's reagent also attacks mercury with the formation of mercurous iodide. According to H. Fleck, mercurous iodide is formed by the action of aluminium amalgam on ethyl iodide; P. Yvon heated a mixture of equimolar proportions of the component elements in a retort to a temp. not exceeding 250°. Mercurous iodide sublimes in red crystals, which become yellow when cold. According to A. Stroman, the product is impure.

(2) *From mercurous salts and iodine or iodides.*—A. Stroman boiled a sat. soln. of mercurous nitrate, feebly acidified with nitric acid—and as free as possible from mercuric salts—along with an excess of iodine; he poured the hot clear liquid into a vessel previously warmed, and cooled it in darkness. The liquid was filtered in darkness, and the mercurous iodide was washed with nitric acid, then with water, and finally dried in darkness at room temp. on filter paper frequently renewed. A. Stroman also used an alcoholic soln. of iodine under similar circumstances. N. E. Henry, and J. B. Berthemot decomposed mercurous nitrate, or chloride with hydriodic acid, or better, with potassium iodide. Since mercurous nitrate requires an excess of nitric acid for its soln. in water, this excess remains free—unless the potassium iodide contains hydroxide or carbonate as recommended by N. E. Henry to neutralize the excess of acid and avoid the formation of mercuric iodide—and an oxidizing action will set in converting mercurous to mercuric iodide; hence, the liquid should be rapidly filtered. The oxidation is more rapid when hydriodic acid is employed than when potassium iodide is used. If the mercurous nitrate is contaminated with mercuric nitrate, mercuric iodide will be formed. If an excess of potassium iodide be used, mercurous iodide will be converted into mercuric iodide which dissolves, and metallic mercury which remains mixed with the precipitate; but a slight excess of potassium iodide is useful in dissolving the mercuric iodide formed by the nitric acid. C. Soetje, R. Varet, and M. François used a similar process. According to M. François, a soln. of mercurous nitrate transforms mercuric iodide into mercurous iodide, and nitric acid dissolves any finely divided mercury which may be present. Hence, he recommends the following preparation:

> Dissolve 125 grms. of mercurous nitrate in 2 litres of water containing 20 grms. of nitric acid; and add a soln. of 50 grms. of potassium iodide in 100 grms. of water, drop by drop, with vigorous agitation. Each drop produces a grey stain which soon becomes yellow. The liquid is agitated 3 or 4 times, while it is allowed to stand 24 hrs. and then decanted from the precipitate, which is then well washed. It is not advisable to wash with alcohol because this liquid decomposes mercurous iodide into the mercuric salt and mercury.

M. François also recommended a soln. of iodine in potassium iodide; F. Bodroux, methyl or ethyl iodide; and P. F. G. Boullay, ferrous iodide. P. C. Ray obtained mercurous iodide as a by-product in the action of ethyl iodide on mercurous nitrite at 190°–210°. Mercurous acetate was used by P. F. G. Boullay in place of the

nitrate, but mercurous acetate is but sparingly soluble in cold water, and it is decomposed by hot water into soluble mercuric acetate and mercury. J. B. Berthemot, therefore, pointed out that it is best to triturate solid mercurous acetate in the cold with an aq. soln. of potassium iodide. A greenish-black powder is first produced, but this soon becomes yellowish-green. The product is liable to be contaminated with undecomposed mercurous acetate which cannot be extracted by cold water, and is resolved by hot water into soluble mercuric acetate and metallic mercury, which remains mixed with the mercurous iodide. J. Lefort recommended a soln. of one part of mercurous acetate, and two parts of sodium pyrophosphate in 10 parts of warm water in place of a soln. of mercurous acetate alone. The mercurous iodide was precipitated by the addition of a soln. of one part of potassium iodide. J. Inglis recommended triturating 235·4 parts of mercurous chloride with an aq. soln. of 165·2 parts of potassium iodide ; if the mercurous chloride be in excess, it remains undecomposed ; and leads to the separation of metallic mercury. O. Lichtenberg said that the product is contaminated with mercurous chloride and mercury.

(3) *From mercuric iodide.*—J. B. Berthemot prepared mercurous iodide by triturating 226 parts of mercuric iodide with 100·6 parts of mercury—preferably with the addition of a little alcohol. T. Rieckher used a similar process. M. François claimed that mercurous iodide of a very high degree of purity can be made by the following process :

> Dissolve 50 grms. of mercuric iodide in a heated mixture of 100 grms. of aniline and 20 grms. of alcohol. Crystals of diphenyldimercuriammonium iodide are deposited on cooling. On adding ether to the mother liquid, acicular greenish-yellow crystals of mercurous iodide are deposited. The preparation depends on the reducing action of a small amount of aldehyde present in ether—for a soln. of aldehyde in 1000 parts of alcohol precipitates mercurous iodide from a soln. of mercuric iodide in aniline.

B. D. Steele noticed the formation of mercurous iodide when a soln. of potassium iodide in liquid sulphur dioxide is electrolyzed using a mercury anode. J. W. Clark prepared mercurous iodide by the electrolysis of molten mercuric iodide with graphite electrodes.

A. Lottermoser prepared *colloidal mercurous iodide* by the action of iodine water on colloidal mercury. According to the patented process of the Chemische Fabrik von Heyden, 20 parts of albumen albuminose peptone, or white of egg, are dissolved in 500 parts of water, and added to a soln. of 17 parts of potassium iodide in 100 parts of water, and the mixture is then stirred with 26 parts of mercurous nitrate in 2000 parts of water, and the yellow soln. dialyzed. The greenish-yellow powder is soluble in water, forming a neutral yellowish-green soln. It is precipitated from the aq. soln. by alcohol, acetone, or acids. The precipitate by alcohol or acetone is directly soluble in water, but the precipitate by acids requires neutralization with an alkali before it is soluble. J. Hausmann has studied the precipitation of mercurous iodide in the presence of gelatine.

The properties of mercurous iodide.—The older chemists—J. Inglis, P. F. G. Boullay, J. B. Berthemot, etc.—described the **colour** of mercurous iodide as yellowish-green or green, and later, when yellow varieties were prepared, R. Varet[3] suggested that this compound occurs in two allotropic states—yellow and green—and he actually measured what he regarded as the heat of transformation from the green to the yellow—0·15 Cal. M. François says that purified mercurous iodide is as yellow as lead chromate, the green colour appears only when very finely divided mercury is present ; the green colour is the resultant effect of the superposition of the colour of mercury on that of mercurous iodide. This is shown by the variations in the tint with different modes of preparation ; analyses of the green specimens show an excess of mercury over that required for mercurous iodide ; the purer the specimen the more it inclines to yellow ; the yellow samples can be made green by charging them with finely divided mercury—say by adding a little potassium iodide to mercurous iodide ; and the green specimens can be made yellow by

dissolving out the mercury—with dil. nitric acid; or by converting the mercury into mercurous iodide by digesting it with a soln. of iodine in potassium iodide. The fact that the properties attributed to mercurous iodide by the older chemists really referred to a mixture of that salt contaminated with a little finely divided mercury renders it necessary to accept many of their statements with some reserve.

According to A. des Cloizeaux, the **crystals** obtained by sublimation are tetragonal (P. Yvon said rhombic) plates with the axial ratio $a:c=1:1{\cdot}6726$ probably, and isomorphous with the crystals of mercurous chloride. According to E. J. Houston, when the light yellow salt is heated, it gradually darkens as the temp. rises, becoming dark yellow, orange, and orange-red; and on cooling these colours appear in the reverse order; at 100°, A. Stroman said that the salt is always yellow. In sodium light, P. Yvon found the pale green colour changed to red at 70°, and at 220°, garnet red. B. Gossner obtained a specimen of mercurous iodide, by the trituration of mercuric iodide and mercury, which turned red abruptly when heated. It is, therefore, assumed that the red form is stable at the higher temp., the yellow at ordinary temp.; that the salt is dimorphous; and that the tetragonal form of the crystals is retained as the salt passes into the yellow modification. According to C. J. B. Karsten, the **specific gravity** is 7·6445; and, according to P. F. G. Boullay, 7·75.

The crystals sublime when heated, and, according to A. Stroman,[4] the sublimation begins between 110° and 120° (P. Yvon says 190°), and increases in velocity with rise of temp.; P. Yvon says the crystals melt to a black liquid, the **melting point** being 290°, with partial decomposition, and the **boiling point** is about 310°. L. Troost measured the **vapour density** between 752 and 754 mm., and found a mean value 15·2—the theoretical value is 15·7. The mol. wt. calculated by E. Beckmann from the depression of the f.p. of molten mercuric iodide agrees with Hg_2I_2, H. V. Regnault's value for the **specific heat** between 17° and 99° is 0·0395; and E. Goldstein gives for the **molecular heat** 6·4.

The **heat of formation** from solid mercury and iodine is (Hg, I) 23·8 Cals., according to M. Berthelot;[5] 24·22 Cals., according to J. Thomsen; and from liquid mercury and solid iodine, according to R. Varet, 28·85 Cals. for the yellow amorphous solid; 28·55 Cals. for the greenish-yellow; and for the yellow salt from liquid mercury and solid yellow mercuric iodide, 6·65 Cals. The **free energy** of formation at 18° is —26·8 Cals. calculated by M. de K. Thompson. J. Thomsen also gives $(HgNO_{3aq.}, KI_{aq.})=21{\cdot}26$ Cals.; $(Hg_2O, 2HI_{gas})$, 86·68 Cals.; and R. Varet, $Hg_2O_{precipitated}+2HI_{soln.}=2HgI_{yellow}+49{\cdot}25$ Cals.

A. des Cloizeaux[6] reported that mercurous iodide crystals exhibit a strong positive double refraction, and J. A. Wilkinson found the salt exhibits a reddish-brown or orange fluorescence. A. L. Hughes has studied the photo-electric effect. S. Bugarszky measured the free energy of the reaction: $2HgCl_{solid}+2KI_{soln.}=2HgI_{yellow}+2KCl_{soln.}$ from the e.m.f. of the cell $Hg \mid Hg_2Cl_2$, $\frac{1}{100}N$-KCl $\mid$ N-KNO_3 $\mid$ $\frac{1}{100}N$-KI, $Hg_2I_{2yellow}Hg$, and found for temp. 0°, 18·5° and 43·4°, the respective values $\epsilon=0{\cdot}3131$, 0·3086, and 0·3117 volt; $d\epsilon/dT=-0{\cdot}00027$. The free energy is therefore 7134 cals., the bound energy 1819 cals., the total energy 8953 cals.; and the observed value of $Q=9310$ cals. For the free energy of the reaction: $2HgCl_{solid}+2KI_{soln.}=2HgI_{greenish\text{-}yellow}+2KCl_{soln.}$, from the e.m.f. of a similar cell with greenish-yellow mercurous iodide substituted in place of the yellow salt, for temp. 0°, 18·5°, and 43·3, the respective values $\epsilon=0{\cdot}3131$, 0·3083, and 0·3017 volt; $d\epsilon/dT=-0{\cdot}000265$. The free energy is therefore 7127 cals., the bound energy 1786 cals., the total energy 8913 cals., and the observed value of Q, 9160 cals. Hence, owing to the agreement between the free and bound energies with the yellow and greenish-yellow salts, it is inferred that these two forms of mercurous iodide are *chemisch identisch*. S. Bugarszky also gives for the energy of the reaction: $Hg_2(C_2H_3O_2)_{2solid}+2KI_{soln.}=Hg_2I_{2yellow}+2K(C_2H_3O_2)_{soln.}$, calculated from the cell $Hg \mid Hg_2(C_2H_3O_2)_2$, N-$KC_2H_3O_2$ $\mid$ N-$KC_2H_3O_2$ $\mid$ $\frac{1}{100}N$-KOH, $Hg_2O \mid Hg$, where he found for 0° and 18·5° the respective values $\epsilon=0{\cdot}4498$ and

0·4277 volt; and $d\epsilon/dT = -0·00118$, the following values: free energy, 9883 cals.; bound energy, 7951 cals.; total energy, 17834 cals.; and Q observed=17,275 cals, F. Braun estimates that 41 to 50 per cent. of the heat of formation can be transformed into electrical energy.

R. Varet[7] says that highly purified mercurous iodide is very little changed when kept away from light; but, according to W. Artus, when mercurous iodide is exposed to **light**, it becomes dark green and finally black, but these changes occur only if the compound is moist, and he adds that no free iodine is then evolved, but hydrogen iodide is given off, and therefore mercurous oxide is probably formed; and, according to J. Inglis, when kept a few weeks in vessels containing air, in darkness, mercury and mercuric iodide are formed in dentritic excrescences—he adds that the decomposition, however, does not take place under water. J. M. Eder says that mercurous iodide blackens in light even if oxygen and moisture are excluded, and he wrongly supposed that mercurosic iodide, Hg_2I_3, is formed. P. Yvon exposed crystalline mercurous iodide for eight years in a flask closed by a sheet of paper, and found it had become almost black; the blackened iodide had lost 0·44 per cent. of mercury; and some crystals of red mercuric iodide collected in the upper part of the flask. A. Stroman found that the precipitated salt is more sensitive to light than the crystalline salt.

A. Mailfert found **ozone** converted mercurous iodide into an oxyiodide. By heating a mixture of mercuric oxide and mercurous iodide obtained by dropping alcoholic potassium hydroxide into a boiling alcoholic soln. of mercuric iodide, with water in a sealed tube at 160° for 80 hrs., and floating off the unchanged mercuric oxide and mercurous iodide, T. Fischer and H. von Wartenberg prepared brownish-red rhombic plates of **tetramercurous trioxyiodide,** $3HgO.HgI$, which, when heated in an open tube and when treated with acids or alkalies, behaves like a mixture of the primary constituents.

According to F. Labouré, when mercurous iodide is sublimed it is resolved into metallic mercury which collects at the top, and a greenish-yellow sublimate below—he wrongly supposed that mercurosic iodide, Hg_2I_3, is formed; P. Yvon says that when heated very quickly an oxyiodide, $6HgO.7HgI_2$, sublimes; while A. Stroman, and M. François say that mercurous iodide cannot be melted without decomposition, and that a mixture of mercury and mercuric iodide is formed as a sublimate, leaving a residue of mercurous iodide. M. François found that mercuric and mercurous iodides in the mol. proportions 2 : 1 can be melted without decomposition.

According to M. Saladin,[8] 100 c.c. of **water** dissolve less than 0·042 grm. of mercurous iodide. G. Bodländer estimates the solubility to be $2·6\times10^{-8}$; M. S. Sherrill, 3×10^{-10}; and J. F. Spencer, 3×10^{-3}. There is probably some hydrolysis of the iodide, the solubility product $[Hg_2''][I_2']$ is $1·2\times10^{-28}$. According to S. Schlesinger, concentrated **nitric acid** decomposes it into mercuric iodide and nitrate which crystallize as a double salt or mixed crystals on cooling. M. François found a soln. of **mercuric nitrate** enters into a reversible reaction, forming mercurous nitrate and mercuric iodide, $Hg(NO_3)_2+2HgI \rightleftharpoons 2HgNO_3+HgI_2$. According to E. Riegel, **sulphuric acid** at ordinary temp. has no action, but, according to A. Souville, when heated it forms a double salt, $HgSO_4.HgI_2$; and he symbolizes the reaction: $2HgI+2H_2SO_4=HgI_2.HgSO_4+SO_2+2H_2O$. Hydrogen chloride was found by P. Hautefeuille to decompose mercurous iodide but slightly if heated below the sublimation temp., while boiling hydrochloric acid slowly forms mercuric chloride and mercury; according to E. Esteve, **hydrocyanic acid** first transforms mercurous iodide into mercuric cyanide, liberating hydriodic acid: $2HgI+2HCy=HgCy_2+2HI+Hg$; the hydriodic acid then reacts with the liberated mercury reforming mercurous iodide. P. F. G. Boullay found that a boiling soln. of **ammonium or sodium chloride** dissolves a little mercuric iodide, and a little mercury separates—L. Mailhe says the mercurous iodide is converted into mercuric chloride which dissolves. P. F. G. Boullay and F. Labouré found that hydriodic

acid or an aq. soln. of a **soluble iodide**—*e.g.* potassium sodium, barium, calcium, magnesium, or zinc iodide—forms soluble mercuric iodide and metallic mercury. A. Stroman noted that **potassium iodide** colours mercurous iodide green in the cold, and black when heated; but, according to M. François, a dil. soln. of potassium iodide changes the green colour to yellow, $2HgI+2KI \rightleftharpoons HgI_2.2KI+Hg$; the reaction is reversible; similarly, with hydriodic acid, but if the acid be concentrated, there is a violent reaction between the hydriodic acid and the mercury formed in the early stages of the reaction. No gas is evolved if the hydriodic acid be dil. more than 97·14 grms. per 100 c.c. of liquid and there is a reversible reaction: $2HgI+HI_{aq.} \rightleftharpoons HgI_2+Hg+HI_{aq.}$ The hydriodic acid dissolves mercuric iodide and the soln. attacks the liberated mercury. For equilibrium, 100 c.c. of liquid contain in grams:

HI	1·142	2·214	4·062	8·272	16·167	28·682	49·807	67·099
HgI_2	0·3405	1·2485	3·518	8·853	20·815	47·670	91·559	118·720

F. Jander found mercurous iodide is more soluble in soln. of **ammonium iodide** than in water—if S_0 be the solubility in water, and S the solubility in a soln. of ammonium iodide with 0·1, 0·25, 0·5, and 1·0 mol per litre, $S-S_0$ is respectively 0·0492, 0·131, 0·236, and 0·549, and the ratio of the conc. of ammonium chloride to $(S-S_0)$ lies between 1·8 and 2·0. It is thought that the soln. contains the complex HgI_2NH_2I or NH_4HgI_3. Similar results were obtained with soln. of potassium iodide by R. Abegg and F. Jander. According to M. François, 20 c.c. of a normal soln. of potassium iodide with 6·54 grms. of potassium iodide are in equilibrium when the soln. has 2·38 grms. of mercuric iodide and the mercurous iodide becomes green; with 20 c.c. of the potassium iodide soln. and 2 grms. of mercurous iodide at 20°, all is converted into mercuric iodide and mercury. According to E. C. Franklin and C. A. Kraus, mercurous iodide is very easily soluble in liquid **ammonia**. G. C. Wittstein found it to dissolve in aqua ammonia, leaving a grey residue—probably globules of mercury; and M. François says that it transforms mercurous into mercuric iodide, and finally, according to H. Saha and K. N. Choudhuri, into white mercuric diammino-iodide, $HgI_2.2NH_3$. M. François also noted that aqua ammonia or alkali-lye transforms mercurous iodide into a green mass, which then blackens, and the corresponding iodide of ammonium or alkali is formed. C. F. Rammelsberg obtained what he regarded as dimercuriammonium iodide, Hg_2NI, from the mother liquid remaining after aqua ammonia had been allowed to act on mercurous iodide. R. Behrend found that mercurous iodide is but slightly affected by dil. aqua ammonia, and he measured the e.m.f. of ammonia soln. in contact with this salt.

M. Saladin said that mercurous iodide is insoluble in *ethyl alcohol*; H. Maclagan says it is not quite insoluble therein, and M. François says that boiling alcohol forms mercury and mercuric iodide until there is present 0·220 grm. of mercuric iodide per 100 grms. of alcohol when the system is in equilibrium, for the reaction is reversible. H. Saha and K. N. Choudhuri report that *methyl alcohol* forms no mercuric iodide. Unlike mercuric iodide, says M. François, mercurous iodide is insoluble in cold *ether*, but H. Maclagan adds that it is not completely insoluble in this menstruum. Mercurous iodide is slightly decomposed by *chloroform*. J. H. Mathews found the specific conductivity of a sat. soln. of mercurous iodide in *allyl mustard oil* to be $4·3 \times 10^{-5}$ at 25°. J. W. Retgers says mercurous iodide is virtually insoluble in *methylene iodide*. M. François found that mercurous iodide is decomposed by *phenol*, with which it reacts reversibly; similar remarks apply to *aniline*.

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§ 24. Mercuric Iodide

Mercuric iodide exists in two forms—red and yellow. It occurs in nature as the mineral *coccinite*, reported by A. del Rio [1] in reddish-brown particles in some mercury ores at Cases Viejas (Mexico), but A. del Castillo has stated that the specimens labelled by A. del Rio contained no iodine. There is, therefore, some doubt about this mineral. J. Domeyko described some *minerales de plata clorojodurados mercuriales* from Caraceles (Chili) with 10·5 to 13·96 per cent. of iodine ; 5·3 to 13·65 per cent. chlorine ; 9·2 to 20·5 per cent. of mercury ; and 16·9 to 40·65 per cent. of silver.

The preparation of mercuric iodide.—B. Courtois [2] prepared vermilion-coloured mercuric iodide by agitating the two elements together in the cold. L. N. Vauquelin made it by triturating the two elements moistened with a little water.

J. B. Berthemot made mercuric iodide by triturating together mercury and iodine in atomic proportions, Hg : I=1 : 2. According to F. Mohr, the combination is not complete because free iodine and mercurous iodide are formed. The union is more complete if water or alcohol be present; if too much alcohol be employed, the temp. rises, the mass fuses, and some iodine is evaporated. J. B. Dublanc recommended pouring a kgrm. of alcohol on 100 grms. of mercury; adding 124 grms. of iodine in successive portions of 10 grms.; and agitating the mixture after each addition until the alcohol becomes colourless. The alcohol remains coloured after the last addition of iodine because all the mercury is then converted into mercuric iodide. The red product is washed with alcohol and dried.

L. N. Vauquelin made the same salt by triturating iodine with mercurous oxide, mercurous nitrate, or mercuric nitrate—some iodate is said to be formed in the last-named reaction.

When a soln. of mercuric chloride, nitrate, or acetate is mixed with an aq. soln. of iodine, C. F. Schönbein noted that a peculiar compound with mercury is formed—possibly a hypoiodite—with the characteristic smell of iodine, and the reaction with starch no longer appears. E. Schaer observed a similar result with chlorine and bromine water.

X. Landerer used mercurous chloride; M. C. Schuyten, mercuric chloride; E. Soubeiran, mercurous iodide, or mercuric cyanide; and J. Schröder used mercury or a mercurous salt and washed the product with pyridine—mercurous sulphate and chromate do not react with the iodine satisfactorily. C. F. Rammelsberg boiled mercuric oxide with iodine and water. F. Gramp heated mercuric chloride with iodine in a sealed tube at 250° for 6 hrs.; E. Soubeiran heated mercurous iodide with arsenic iodide when the latter compound is reduced to arsenic. According to E. P. Perman, if the mercuric chloride and potassium iodide be finely powdered, and thoroughly dried over phosphorus pentoxide, the red coloration indicating the formation of mercuric iodide does not appear.

When mercury is treated with hydriodic acid, mercuric iodide is formed and hydrogen evolved; and, according to R. S. Norris and F. G. Cottrell, this more readily than is the case when mercuric bromide is formed by the action of hydrobromic acid on mercury. P. F. G. Boullay made mercuric iodide by precipitation from aq. soln. of mercuric nitrate or chloride with hydriodic acid, or a soln. of potassium or ferrous iodide and washing the product with water; he added that unless the materials are mixed in eq. proportions, part of the mercuric iodide remains dissolved either in the excess of mercuric salt or the potassium iodide.

H. Köhler also recommended suspending 10 grms. of iodine in water, and adding iron filings until all the iodine is changed to ferrous iodide; this soln. is immediately poured into one containing 10·75 parts of mercuric chloride. The precipitated mercuric iodide is rapidly separated from the mother liquid to avoid contamination with iron oxychlorides. The precipitate is washed with cold water and recrystallized by cooling a soln. of the salt from a hot soln. of potassium iodide or hydrochloric acid. The red lustrous crystals have a greenish reflection.

M. François treated mercury with a soln. of iodine and potassium iodide. F. R. Williams made mercuric iodide by precipitation from a soln. of four parts of mercuric chloride and two parts of ammonium chloride by five parts of potassium iodide. W. Sievers boiled a soln. of mercuric nitrate with iodine. C. F. Schlagdenhauffen heated mercuric chloride with ethyl iodide in a sealed tube at 100°; F. Bodroux agitated an aq. soln. of mercuric acetate with methyl iodide for 12 hrs.; M. C. Schuyten exposed a mixture of mercuric chloride and methyl iodide in ethereal soln. to sunlight and found mercuric iodide was quantitatively precipitated. E. Rupp and S. Goy treated a soln. of mercuric oxide and cyanide with potassium iodide; and W. O. de Coninck treated a soln. of potassium chlorocyanomercuriate with butyl iodide. A. Ditte treated a conc. aq. soln. of iodic acid with mercury and found that the resulting mercuric iodide is mixed with some iodate. C. Fränkel recommended purifying the salt by recrystallization from a boiling soln. of conc.

hydrochloric acid, and washing the product with cold water. J. Preuss, and E. Riegel studied various methods of preparing this salt. A. Lottermoser prepared colloidal soln. of mercuric iodide by the action of a soln. of iodine on colloidal mercury; and J. Hausmann studied the formation of mercuric iodide in soln. of gelatine.

In 1827, P. F. G. Boullay [3] described what he regarded as *un iodure de mercure intermédiaire*, formed by adding a soln. of potassium iodide or hydriodic acid to mercurous nitrate, and not collecting the precipitate until the colour has changed to yellow; and also by dissolving in a soln. of potassium iodide an amount of iodine eq. to half that contained in the salt, and adding the soln. to one of mercurous nitrate. The red precipitate first formed becomes yellow on agitation. If too much iodine soln. has been added, mercuric iodide is formed, and this may be removed by washing with alcohol. J. M. Eder also supposed this salt is formed by the action of light on moist mercurous iodide. J. L. Gay Lussac and J. J. Colin supposed the yellow product to be mercurous iodide, but J. Inglis, P. F. G. Boullay, etc., showed that it contains more iodine than mercurous iodide, and P. F. G. Boullay regarded it as *mercurosic iodide*, Hg_2I_3. M. François, however, showed that the product is really a mixture of mercurous and mercuric iodides which can be separated by extraction with ether.

The properties of mercuric iodide.—In 1833 E. Mitscherlich [4] demonstrated that mercuric iodide exists in two allotropic forms—a red tetragonal form which is stable and is obtained by crystallization from soln. at ordinary temp.; and a yellow rhombic form which is not stable and is obtained by sublimation or by crystallization from the molten salt. According to W. C. Luczizky, the axial ratios of the yellow rhombic **crystals** are $a : b : c = 0{\cdot}62688 : 1 : 1{\cdot}7893$; and of the red tetragonal crystals $a : c = 1 : 2{\cdot}0080$. E. Taubert, P. Groth, W. C. Luczizky, H. Köhler, E. Mitscherlich, and A. Oppenheim, have obtained ditetragonal bipyramidal crystals of different habits from hydrochloric acid, methyl and ethyl alcohols, acetone, allyl iodide, benzene, etc., and aq. soln. in presence of mercuric chloride or bromide, or potassium iodide. According to P. Groth, the crystals from benzene or potassium iodide soln. are normally uniaxial, but from acetone soln. the crystals are for the most part anomalous in appearing biaxial. J. H. Kastle found that at —190° the red variety becomes orange-yellow, and the red form is white. J. Dewar found that in liquid air, red mercuric iodide is yellow, and in liquid hydrogen white—the original colour returns when the atm. temp. is restored; D. Dobrosserdoff found that when cooled by solid carbon dioxide, red crystalline mercuric iodide becomes yellow, and he stated that the change is due neither to dissociation nor to modifications in the structure of the mol.

The yellow crystals obtained by sublimation may retain their yellow colour when cooled, or they may become scarlet-red. If the yellow colour is retained, the red colour is very quickly resumed when the crystals are mechanically agitated by rubbing, stirring, or scratching with a pointed instrument. The part so treated becomes scarlet, and, according to A. A. Hayes, "this change of colour extends with a slight motion throughout the whole mass of adherent crystals as if the mass were alive. During this change the crystals retain their form unchanged and are therefore pseudomorphic"; and R. Warington added that under the microscope the red coloration extends through the yellow plates by sudden starts, and is bounded by a line parallel to a lateral face or to a diagonal. C. Strzyzowsky has also examined the formation of mercuric iodide microscopically. W. W. Mather noted that the fused mass exhibits a red colour immediately after solidification, but very rapidly turns yellow. The same crystals turn yellow every time they are heated and red again on cooling. On cooling, however, the crystals may remain yellow for several days. W. Spring also noted that press. transforms yellow mercuric iodide into the red variety. G. Tammann prepared a colourless modification of mercuric iodide by heating mercuric iodide to 300°–500° in a long glass tube connected with a receiver in which the press. can be suddenly reduced from one to one-tenth atm. The colourless snow-like mass so obtained becomes pink in a few seconds, and red after some minutes. If the receiver is cooled to

a low temp. the white form persists longer. Yellow mercuric iodide appears white if cooled to the temp. of liquid air, but this white form is not identical with the other.

A. Oppenheim first determined the **transition temperature** by heating the iodide in capillary tubes. He found 148°–154°, and added that the result is dependent on the quantity of substance employed, and on the diameter of the capillary. He regarded 148° as the most probable value. H. Köhler gave 150°. W. Schwarz showed that the transition point is 126·3°; G. F. Rodwell and D. Gernez gave 126°; A. Smits, and A. Steger, 127°; W. Reinders, 127·2°; J. S. van Nest, and C. Sandonnini, 128°; J. Guinchant, 130°; and M. Padoa and C. Tibaldi, 131·9°. Consequently, at normal press., the yellow variety is stable above 128°, and the red form is stable below 128°. The red in general changes to the yellow form sharply on passing through 127°, but on cooling the yellow colour may persist for several hours, showing that the red form cannot be much superheated, but the yellow form can be considerably undercooled. The transformation from yellow to red mercuric iodide proceeds very quickly in presence of a crystal of the red variety. W. Schwarz noted that the transformation temp. is raised 1·1° by a press. of 100 atm. According to W. Reinders, the transition temp. is lowered by admixture with mercuric bromide as illustrated in Fig. 25; and, according to M. Padoa and C. Tibaldi, by admixture with mercuric chloride. A. Steger found the transition point is raised from 127° to 132° by silver iodide.

P. W. Bridgman studied the effect of press. on the transition point of mercuric iodide, and found that it rose to a maximum when the press. approximates to 5000 kgrms. per sq. cm. as illustrated in Fig. 24, and in Table X. The latter also shows the change in vol., δv in c.c. per gram in passing through the transition point; the change in the transition temp. per unit change of press. dT/dp; the latent heat in kilogrammetres per gram; and the change of internal energy in kilogrammetres per gram.

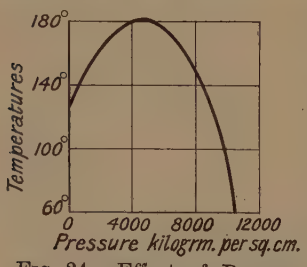

Fig. 24.—Effect of Pressure on the Transition Temperature of Mercuric Iodide.

According to W. C. Luczizky, light yellow crystals of approximately $HgI_2+2HgBr_2$ are obtained by slowly cooling a soln. of mercuric iodide in a warm sat. soln. of the bromide, the axial ratios of the crystals are $a:b:c=0{\cdot}6782:1:1{\cdot}7878$; and from a soln. of $HgI_2+6HgBr_2$, crystals of the composition $HgI_2.2\frac{1}{2}HgBr_2$ with axial ratios $a:b:c=0{\cdot}6718:1:1{\cdot}7222$ are also formed. P. Groth found a mixture with approximately HgI_2+HgBr_2 has the axial ratios $a:b:c=0{\cdot}6443:1:1{\cdot}8389$. J. S. van Nest obtained an unbroken series of yellow mixed

Table X.—Effect of Pressure on the Transition Point of Mercuric Iodide.

Pressure. Kilograms per sq. cm.	Transition Temperature.	δv c.c. per gram.	dT/dp.	Latent heat in kilogrammetres per gram.	Change of internal energy in kilogrammetres per gram.
1	127·0°	0·00342	0·0267	0·513	0·513
1000	149·8°	0·00217	0·0187	0·491	0·469
2000	165·2°	0·00127	0·0122	0·456	0·431
3000	174·9°	0·00065	0·0069	0·420	0·400
4000	179·9°	0·00024	0·0028	0·390	0·380
5000	181·2°	−0·00008	−0·0010	0·365	0·369
6000	178·2°	−0·00045	−0·0059	0·345	0·372
7000	169·7°	−0·00100	−0·0134	0·330	0·400
8000	152·4°	−0·00175	−0·0234	0·318	0·458
9000	122·3°	−0·00270	−0·0361	0·296	0·539
9500	102·4°	−0·00325	−0·0427	0·286	0·594
10000	79·4°	−0·00390	−0·0495	0·278	0·668

crystals with up to 97 per cent. mercuric iodide; while if less than 3 per cent. of mercuric bromide be present, only red crystals are formed. Red mixed crystals can also be obtained with up to 50 per cent. mercuric iodide. W. Reinders and P. Niggli also obtained an unbroken series of yellow rhombic crystals by cooling molten mixtures of the two salts. The fusion curve corresponds with H. W. B. Roozeboom's curve Type III—mercuric bromide fuses at 236°, the iodide at 255°, and the minimum with about 41 per cent. of mercuric iodide at 216·7°.

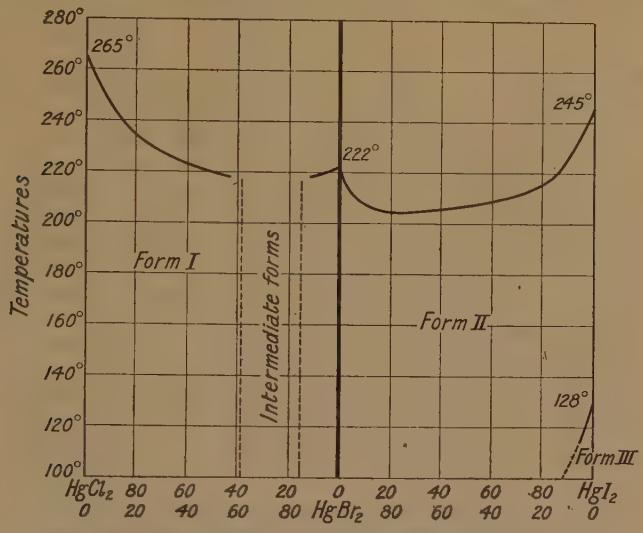

Fig. 25.—Fusion Curves of Binary Mixtures of Mercury Bromide with Mercury Chloride and Iodide.

J. S. van Nest's curves for binary mixtures of mercury bromide with the iodide and chloride are shown in Fig. 25.

The transition point of the yellow to red form is lowered by admixture with mercuric bromide as illustrated in Fig. 26. The effect is represented by two curves between which lies a transition interval so that on one side only the α- or red crystals, and on the other side only the β- or yellow crystals, can exist. The fall of the curve is so very steep that the corresponding transition point for mercuric bromide, if it exists at all, must be below —83°. The yellow mixed crystals are also more stable at ordinary temp. than is the case with the yellow iodide alone, and this the more the larger the proportion of the bromide, as was observed by N. S. Kurnakoff and P. P. Ejler, and by G. Bruni and M. Padoa.

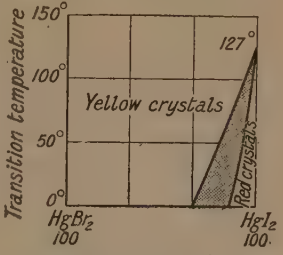

Fig. 26.—Effect of Mercuric Bromide on the Transition Temperature of Mercuric Iodide.

There is not so complete a series of mixed crystals between mercuric chloride and iodide as between the bromide and iodide. M. Padoa and C. Tibaldi obtained a V-shaped f.p. curve with a minimum at 145° with 48 per cent. of mercuric iodide. There is a gap in the series of mixed crystals with between 50 and 70 per cent. of mercuric chloride. The mixed crystals are red at ordinary temp., excepting only those with 1·3 molar per cent. of the iodide. The lowering of the transition temp. with the chloride is not so great as with the bromide. The mercuric halides are isotrimorphous in that they present three crystalline forms: (i) the rhombic form of the chloride—not isomorphous with that of the bromide; (ii) the rhombic form of the bromide; and (iii) the tetragonal form characteristic of the red iodide. The

bromide crystallizes with the chloride in the first form, and with the iodide in the second and third forms. A. Steger prepared mixed crystals of mercuric and silver iodides by melting and solidifying mixtures of the two salts. There is a gap in the series between 5 and 20 mols. per cent. of silver iodide. The mixed crystals with up to 5 mols. per cent. of silver iodide are of the rhombic mercuric iodide type; and those with upwards of 20 mols. per cent. are of the regular silver iodide type.

G. Wyrouboff wrongly supposed that the red and yellow iodides furnish each its own characteristic vapour, and that the vap. densities of the red iodide is greater than that of the yellow. It was thought that yellow mercuric iodide is formed by rapid condensation of the vapour, but that if the sublimation occurs at a low temp. red crystals may be obtained. D. Gernez has shown that in every case it is very probable that the yellow form is first deposited and that this subsequently becomes red. D. Gernez observed that even when the red salt is vaporized, yellow crystals are first formed by condensation from the vapour at temp. as low as 25°. M. L. Frankenheim noted that when a mixture of the red and yellow iodide is heated on a glass plate and allowed to condense on another plate held a short distance above, the sublimate is a mixture of both iodides. M. Berthelot, however, does not regard this as proving the existence of red iodide in the state of vapour because solid particles of the red iodide are projected mechanically from the lower plate to the upper, and convert the yellow iodide condensed in their immediate vicinity into the red. If either red or yellow mercuric iodide be vaporized in vacuo, at a relatively low temp., and a cooler solid is introduced, yellow crystals are deposited if the surface be thoroughly clean, but if the solid has been rubbed at one spot with a crystal of the red variety and a crystal of the yellow variety at another spot, D. Gernez showed that red crystals are deposited on the former, and yellow crystals on the latter.

When a mercuric salt is treated with potassium iodide, a pale yellow precipitate separates out, and this immediately becomes scarlet-red. According to R. Warington, under the microscope, the precipitate which is first formed with mercuric chloride appears to be composed of rhombic laminæ, which are yellow by reflected light; these crystals gradually alter by the truncation of the edges and corners as if they were dissolving, and their dimensions are reduced until red square-based octahedrons are produced. R. Warington, and M. Berthelot also noted that if an alcoholic soln. of mercuric iodide be treated with water, or if a hot sat. alcoholic soln. be cooled, crystals of the yellow iodide are formed. According to L. Selmi, if an alcoholic soln. of mercuric iodide be poured into water, a yellow emulsion is formed from which yellow rhombic plates separate in a few hours; in agreement with the general behaviour of colloidal suspensions, M. L. Frankenheim and others noted that during the precipitation of salts by alcohol, an unstable liquid phase is first formed, and from this the salt then separates. The emulsion is quickly flocculated by the addition of acids or neutral salts. L. Selmi also found sulphuric acid acts like water; with nitric acid, yellow and red mercuric iodides are precipitated; and with hydrochloric or acetic acid, only the red iodide. H. Schiff, and A. Reynoso also made observations on the separation of mercuric iodide from alcoholic soln. It is probable that the yellow iodide is in all cases precipitated, and that the precipitate is more or less rapidly converted into the red iodide in the presence of different catalytic agents.

Analogous results have been reported with soln. of red and yellow mercuric iodides in methyl alcohol (W. D. Bancroft, and P. Rohland); in methylene iodide (J. W. Retgers); nitrobenzene, *m*- and *p*-nitrotoluene, *o*-nitronaphthalene (L. Mascarelli); alcohols, hydrocarbons, hydrocarbon halides, ethers, esters, aldehydes, ketones, organic acids and anhydrides, phenolamines, hydrazides, quinoline, pyridine (D. Gernez); allyl alcohol, amyl alcohol, acetone, phenol, benzene, toluene, naphthalene, ψ-cumene, propionitrile, isopropyl or isobutyl bromide, ethylidene chloride, ethyl and phenyl cyanides, benzoic acid, ethyl acetate, propionate, butyrate, *i*-butyrate, iodide, or bromide; propyl chloride, isobutyl bromide, methyl and

phenyl salicylate (J. H. Kastle and M. E. Clark). E. Beckmann and A. Stock report that the soln. of mercuric iodide in chloroform is violet; in benzene, red; and in ether, acetone, ethyl or methyl alcohol, brown; but the soln. are in general yellow and furnish yellow crystals when the hot sat. soln. is cooled; the pink colour of certain soln.—*e.g.* with isobutyl bromide or propyl chloride—is attributed by J. H. Kastle and M. E. Clark not to the presence of red mercuric iodide, but to the formation of unstable alkyl or similar iodides. Soln. of mercuric iodide in molten naphthalene or spermaceti are colourless, but become yellow if rapidly cooled, and red if slowly cooled below the transition temp. 127°. According to Lüppo Cramer, the presence of gelatine in the soln. favours the formation of the yellow iodide; and W. Ostwald stated that when precipitated from alcoholic soln. in the presence of a colloid, presumably gelatine, the yellow form of mercuric iodide can be preserved a long time. J. N. Friend also showed that in general protective colloids or organic emulsoids retard the velocities of chemical or physical reactions which involve a change of state in one or more of the components. For instance, in the precipitation of mercuric iodide from soln. of mercuric chloride and potassium iodide, the unstable yellow form first precipitated rapidly assumes the stable red form; but in the presence of one per cent. of gelatine, there is a momentary formation of colloidal iodide, and the canary-yellow precipitate which follows remains unchanged for half an hour. As indicated by W. Ostwald, R. Weber, H. Schiff, A. Reynoso, L. Selmi, etc., the change is accelerated by exposure to light.

L. Mascarelli found only one value for the solubility with both the red and yellow iodides at a definite temp., and that the solubility curves are continuous between 0° and 230° without the appearance of any break at the transition point of the red to the yellow iodide. Hence it is inferred that the yellow form alone exists in soln. at all temp. The yellow form separates in all cases, but below the transition temp. the yellow form persists for a length of time, depending on the distance of the temp. below the transition point. The yellow form of mercuric iodide which separates by cooling, say, a soln. of this salt in amyl alcohol from 150° to 118°, begins to develop spots of the red iodide in about 10 mins. W. W. Mather noted that potash-lye immediately turns the yellow iodide red. J. H. Kastle and J. V. Reed found the stability of the yellow iodide to vary greatly under different solvents. As a rule, the stability increases with the viscosity of this solvent, and is greater under vaseline than under any other solvent yet examined. In illustration, no change was observed after standing $1\frac{1}{2}$ years under vaseline, the change began under glycerol in 1 to 5 weeks; and under amyl alcohol in 10 mins. W. Reinders also noted the slowness of the change from yellow to red when in contact with viscous liquids. This is in agreement with general experience that chemical and physical changes are slow in viscous solvents. J. H. Kastle and J. V. Reed also found that soln. of mercuric iodide in naphthalene sat. at 140° yield no solid when cooled to 100°; the supersaturated soln. is not usually affected by adding a crystal of the red iodide, but a crop of crystals of the yellow iodide are obtained when the soln. is seeded with a yellow crystal; other substances—*e.g.* powdered glass, gypsum, or dolomite—also lead to the separation of yellow crystals. Where a red crystal does cause a precipitation from yellow soln., yellow crystals are produced.

It almost seems as if the red iodide is insoluble in organic solvents and that the red iodide forms the yellow variety before it dissolves, as is evidenced by the slower rate of soln. of the red variety in naphthalene. W. Ostwald has stated that he considers there is no difference between the gaseous and liquid states of aggregation of different allotropic forms of a solid; the vapour of red phosphorus is identical with the vapour of yellow phosphorus; a soln. of rhombic sulphur in carbon disulphide is no different from a soln. of the monoclinic form; and different forms of many salts are obtained from under-cooled soln.—*e.g.* nickel sulphate—by introducing a fragment of the corresponding crystal. Consequently, physical isomerism occurs exclusively with solids, and disappears when the substance assumes another state of aggregation. So also with mercuric iodide, the same

soln. is obtained whether the red or yellow iodide be used at the start; and similarly also with the vapour. This idea can be symbolized: $HgI_{2gas} \rightleftharpoons HgI_{2liquid} \rightleftharpoons HgI_{2yellow\ solid} \rightleftharpoons HgI_{2red\ solid}$.

J. H. Kastle and M. E. Clark say that the separation of the yellow iodide from soln. appears to indicate that the transition temp. is lowered by the solvent; but the precipitation of the less stable yellow form of mercuric iodide from soln., or from supersaturated soln., or its formation by double decomposition, is usually cited as an illustration of W. Ostwald's generalization that *when a substance leaves any state and passes into another more stable one, the one actually produced is not the most stable one under the existing conditions, but the one which can be reached with the minimum loss of free energy.* For example, of the two possible forms of mercuric iodide the yellow less stable form is the first to appear during sudden precipitation. The theory of the allotropic states of mercuric iodide has been discussed by A. Smits, G. Tammann, M. Hasselblatt, etc.

The reported values [5] for the **specific gravity** of red mercuric iodide vary from H. Schiff's 5·91 to J. S. van Nest's 6·2939 (20°); the latter gave 6·282 (20°) for the yellow iodide. F. W. Clarke's value for the mean of seven determinations is 6·231. According to G. F. Rodwell, the sp. gr. of the red iodide at 0° is 6·2972; and at 126°, 6·276; the sp. gr. of the red iodide at 126° is 6·225; at the m.p. 200°, the sp. gr. of the solid is 6·179, and of the liquid, 5·286. K. Beck gives 5·34 for the sp. gr. of the liquid at 258°; and E. B. R. Prideaux gave for the sp. gr. of the liquid at a temp. θ between 255° and 355°, 5·238–0·00322 (θ—255). W. Biltz gave 72·2 for the mol. vol. of yellow mercuric iodide, assuming the sp. gr. is 6·297 (0°). A. Reis and L. Zimmermann gave 2·0 for the **hardness** on Mohs' scale. The **coefficient of cubical expansion** from 0° to the transition point 126° was found by G. F. Rodwell to be 0·0000344706 per degree for the red iodide; and for the yellow iodide from 126° to 200°, 0·0001002953 per degree. P. W. Bridgman gives the change in the coeff. of thermal expansion with press. as —0·000038 at a press. of one kilogram per sq. cm.; —0·000036 at 2000 kgrms. per sq. cm.; +0·000020 at 6000, +0·000023 at 8000, and +0·000021 at 10,000 kgrms. per sq. cm. The changes in volume which occur between 0° and 200° are illustrated in Fig. 27. According to W. Reinders, the change of volume at the transition temp. is 0·00135 c.c. per gram, and to P. W. Bridgman, 0·00342 per gram as indicated in Fig. 27. The change from yellow to red, during the cooling of mercuric iodide, is accompanied by distinct crackling sounds.

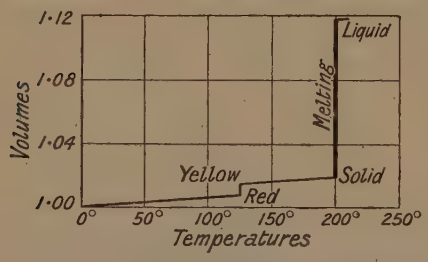

FIG. 27.—Relation between the Volume and Temperature of Mercuric Iodide. —G. F. Rodwell.

H. V. Regnault [6] found the **specific heat** or mercuric iodide between 18° and 99° to be 0·0420; W. Schwarz, between 22° and 131°, 0·0413; J. Guinchant found 0·0406 between 0° and 100°, and for the fused salt, 0·0554; and H. Barschall found between —72·5° and —183·3°, 0·0376; and between —78·2° and —183·3°, 0·0370. At atm. press., the yellow iodide has the larger sp. ht. J. Guinchant gives the difference as 0·0040 cal., but, according to P. W. Bridgman, as the press. increases the difference becomes less. E. Goldstein found the **molecular heat** to be 6·4, and at low temp. down to —183·3°, 17·0. When the iodide is heated above the transition temp. the yellow colour gradually darkens, and just before the m.p. is attained the solid becomes a deep reddish-brown. According to G. F. Rodwell, the **melting point** of the solid is 200°, and, according to A. Oppenheim, 238°, but more recent measurements show that these numbers are much too low—R. Warington, and T. Carnelley and W. C. Williams gave 238° to 238·1°; E. Beckman, 250°; H. Köhler, 253° to 254°; C. Sandonnini, and M. Padoa and C. Tibaldi, 254°; W. Reinders, 255·4°; and A. Smits, 255·5°. J. S. van Nest gave 245° for the m.p.

of the yellow iodide, and 243° for the red iodide. When heated slowly, the yellow colour gradually changes to orange, without a change in the crystalline form, as the temp. approaches 200°, and the molten liquid is dark red. By extrapolation, F. M. G. Johnson estimated the **boiling point** to be 351°. The colour of molten mercury iodide is very like that of bromine. A portion of A. Smits' equilibrium diagram is shown in Fig. 28. The colour of red mercuric iodide persists from S_3 to S_2, because the mols. of the red iodide predominate; at the transition point, S_2 to S_1, there is a change, so that the red mols. preponderate; the change to orange is attended by a gradual increase in the proportion of red mols., and at the m.p., SS_0, the red mols. again preponderate and form a red liquid. The m.p. of the yellow iodide is represented diagrammatically at A.

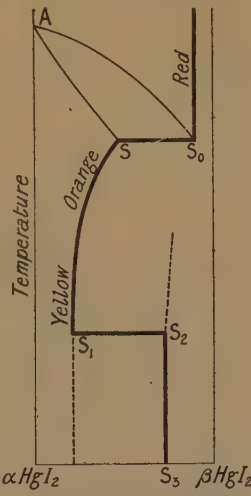

FIG. 28.—Diagrammatic Representation of the Binary System α-HgI_2 and β-HgI_2.

K. Beck found the **viscosity** of molten mercuric iodide at 258° to be 3·963 (water at 25° unity). According to P. W. Bridgman, the coefficient of **compressibility** is 0·00000033 c.c. per gram per kilogram per sq. cm. N. S. Kurnakoff and S. F. Schemtschuschny give the **flow pressure** as 67·8 kgrms. per sq. mm. According to E. Beckmann, the **latent heat of fusion** per gram is 12·4 cals.; J. Guinchant gave 9·79 Cals. at 250°. According to E. Beckmann, the **molecular weight** computed from the lowering of the f.p. of iodine is 463 when the value calculated for HgI_2 is 454. J. Timmermanns obtained higher values indicating a partial association of the mol., but E. Beckmann ascribes this to the use of too high a value for the freezing constant of iodine. F. Garelli and V. Bassani find mercuric iodide has a normal mol. wt. when determined by its action on the f.p. of methylene iodide. W. Herz and M. Knoch found that the raising of the b.p. of alcohol by mercuric iodide corresponds with the normal mol. HgI_2. H. Steiner and J. Schröder found that in soln. of methyl acetate the b.p. method corresponds with a mol. wt. 335 to 404·2—in approximate agreement with a 10 per cent. ionization of the salt. M. Hamers found a mol. wt. of 430·5 in ethyl acetate soln.; A. Werner, 462 in methyl sulphide; 457 in ethyl sulphide; 474 in benzonitrile; and 408 in pyridine; J. Schröder found a mol. wt. of 436 in pyridine soln.; and P. Walden and M. Centnerszwer say that in very dil. pyridine soln. the mol. wt. is normal, and that it decreases slowly with increasing conc.

According to C. Zenghelis, the vaporization of mercuric iodide can be detected at ordinary temp.; V. Borelli also detected it at 80°. H. Saha and K. N. Choudhuri found 2·4359 grms. lost 0·0376 grm. in 12 hrs. at 100°; O. Sulc found a loss of 5·4 per cent. when the finely powdered salt is heated 6 hrs. at 101·5°, and H. Arctowsky found that when heated 5 hrs. at 80°, the salt lost 0·06 per cent.; at 103°, 0·70 per cent.; and at 130°, 4·2 per cent. The **vapour pressure**, p, from 100° to 330° has been determined by E. Wiedemann, K. Stelzner, and G. Niederschulte, and their values below 177°, and F. M. G. Johnson's values above this temp. are:

Temp.	100°	150°	177°	203°	253°	266°	301°	318°	341°
p	0·023	0·79	3·0	10·0	73·0	108	260	390	624

No change in the slope of the curve was observed by F. M. G. Johnson at the m.p., although W. Reinders noted such a change. Vap. press. measurements have also been made by A. Ditte, and by E. B. R. Prideaux. T. Carnelley and W. C. Williams' value for the **boiling point** lies between 339° and 359°; W. Hittorf's value is 358°. F. M. G. Johnson obtained 351° at 760 mm. by extrapolation of the vap. press. curve. L. Rotinjanz and W. Suchodsky found the **critical temperature** to be 1072°, a result in agreement with the value 1077° calculated from T. E. Thorpe and

A. W. Rucker's formula. C. M. Guldberg's ratio T_b/T_c=0·584, where T_b and T_c respectively denote the b.p. and critical temp. in absolute degrees. H. Rassow gave 797° for the critical temp. of mercuric iodide. M. Prud'homme, and E. van Aubel studied the relation between the critical temp., the b.p., and the m.p. According to F. M. G. Johnson, the **heat of vaporization** is 15·84 cals., and, according to E. B. R. Prideaux, 14·7 cals.; and the corresponding values of **Trouton's constant** Q/T are 25·47 and 23·5 respectively. According to **W. Ramsay's rule,** b.p. at T_1 and 750 mm. and at T_2 and 450 mm., the ratio T_1/T_2 is 1·040 for mercuric chloride, 1·043 for the bromide, and 1·042 for the iodide. The molten salt heated in a large glass balloon furnishes a colourless vapour which becomes coloured as the vapour dissociates. H. St. C. Deville noted that the vapour is violet near the walls of the vessel, and colourless nearer the middle, and L. Troost found that the dissociation increases as the temp. rises, so that at 665°, about one-fifth of the vapour is dissociated. H. Debray noted that gold-leaf is whitened and powdered by the dissociating vapour of mercuric iodide. E. Mitscherlich found the **vapour density** to be 15·6 to 16·2; and L. Troost, 15·89 at 17·6°, and 14·9 at 15·4°—the theoretical value is 15·712.

According to J. Thomsen,[7] the **heat of formation** of mercuric iodide from its elements is (Hg, I_2)=34·31 Cals.; (2HgI, I_2)=20·18 Cals.; ($HgCl_{2aq.}$, $2KI_{aq.}$) =26·75 Cals.; (HgO, $2HI_{gas}$)=84·07 Cals. M. Berthelot found $HgO+2HI_{soln.}$ $=HgI_{2red}+46·4$ Cals. and $=HgI_{2yellow}+43·4$ Cals. R. Varet gives Hg_{liquid} $+I_{2solid}=HgI_{2red}+25·2$ Cals., and $=HgI_{2yellow}+22·2$ Cals.; $Hg_{liquid}+I_{2gas}$ $=HgI_{2red}+38·8$ Cals., and $=HgI_{2yellow}+35·8$ Cals. Consequently, as noted by R. Weber, and G. F. Rodwell, heat is absorbed when the red iodide changes to yellow, and evolved when the yellow iodide changes to red. R. Weber found that a thermometer, dipping in the crystals during the change from the yellow to the red iodide, rose by 3° or 3·5°. According to M. Berthelot, the heat of transformation, $HgI_{2yellow}=HgI_{2red}+3·0$ Cals.; W. Schwarz gives 1·1516 Cals.; J. Guinchant, 1·53 Cals. as 130°; and P. W. Bridgman, 1·2 Cals. as indicated in Table X. M. S. Sherrill gives the **free energy** of formation of mercuric iodide from its ions as 48·6 Cals.

The red crystals of mercuric iodide have a strong negative double refraction; according to E. Taubert,[8] the ordinary ray is blood-red, the extraordinary ray, orange-red. G. D. Liveing found soln. of mercuric iodide in potassium iodide have a greater index of refraction than flint glass, or carbon disulphide; for soln. of sp. gr. 2·77, at 18°, he found the **index of refraction** for the *A*-line to be 1·628; *B*-line, 1·637; *C*-line, 1·641; *D*-line, 1·654; *E*-line, 1·673; and for the *F*-line, 1·693. A. Lesure says that the soln. are almost opaque to ultra-violet rays. J. A. Wilkinson found mercuric iodide gives a yellow fluorescence. E. L. Nichols and B. W. Snow measured the reflecting power, i, of mercuric iodide for rays of different wave-length, λ, at different temp.:

λ . . .	0·7530	0·6689	0·6080	0·5570	0·5185	0·4920	0·4500
i at 25° . .	0·895	0·771	0·330	0·050	0·053	0·054	0·055
i at 122° . .	0·846	0·744	0·066	0·046	—	0·044	0·032

According to H. von Jüptner, the red iodide prepared in the wet way appears to be colourless in the light from a sodium flame. A. L. Hughes found the **photo-electric effect** of mercuric iodide to be rather less than that of mercurous iodide. O. Schönrock measured the **electromagnetic rotation** of alcohol and pyridine soln. of mercuric iodide.

B. O. Peirce[9] found the **emission spectrum** of mercuric iodide gave continuous bands with the mid-point about 4430. A. C. Jones extended the results into the ultra-violet, and A. K. Chapman found a wide emission band shading off to the violet and red, and he claimed that there is a definite relation between the emission and absorption spectra, so that the vibrating system responsible for the emission is responsible for absorption in soln. C. Sheard and C. S. Morris found

that with mercuric iodide there are continuous regions or bands between 6072 and 5845; 5605 and 5535; 5195 and 5132; 4828 and 4788; 4506 and 4470; and 4450 and 4375.

According to S. Meyer,[10] the **magnetic susceptibility** of mercuric iodide is $-0{\cdot}26 \times 10^{-6}$ units of mass. W. Beetz measured the **electrical conductivity** of solid mercuric iodide at about 110°; and A. Gockel found that the solid is quite a good conductor between 229° and its m.p. 250°. W. Hampe did not find the yellow solid a conductor. M. Faraday, and J. W. Clark said that the molten iodide conducts electrolytically. W. Beetz added that the molten liquid about the anode is blackened by the separation of iodine, but no mercury appears at the cathode, and accordingly W. Hampe concluded (i) that the mercuric iodide decomposes into iodine and mercury, (ii) the mercury unites with mercuric iodide to form mercurous iodide, and (iii) the mercurous iodide dissolves in the molten electrolyte. J. W. Clark also noted the formation of mercurous iodide during the electrolysis of molten mercuric iodide between graphite electrodes. F. Kämpf found that for low current densities, red mercuric iodide is ten times better conducting in light than in darkness.

F. Kohlrausch and F. Rose have studied the electrical conductivity of aq. soln. of mercuric iodide; and C. Fritsch found the conductivity to be augmented by the addition of one per cent. of potassium iodide. The ionic concentration, in soln. of mercuric iodide: $HgI_2 = HgI^{\cdot} + I'$ is 10^{-7}, and E. Abel emphasizes how very small is the degree of ionization of the salt. H. N. Morse gives for the ionization constants $[Hg^{\cdot\cdot}][I'] = 0{\cdot}4 \times 10^{-13}[HgI^{\cdot}]$; $[HgI^{\cdot}][I'] = 2{\cdot}5 \times 10^{-12}[HgI_2]$; $[Hg^{\cdot\cdot}][I']^2 = 10^{-25}[HgI_2]$; and $[Hg^{\cdot\cdot}][HgI_2] = 0{\cdot}016[HgI^{\cdot}]^2$. M. S. Sherrill gives for the formation of complexes $[Hg^{\cdot\cdot}][I']^4 = 1{\cdot}9 \times 10^{-30}[HgI_4'']_5$ and $[HgI_2][I']^2 = 7{\cdot}3 \times 10^{-5}[HgI_4'']$; he also estimates that in a sat. soln. of mercuric iodide the concentrations of the different kinds of mols and ions are HgI_2, $1{\cdot}3 \times 10^{-4}$; $HgI^{\cdot}$ and I', $1{\cdot}8 \times 10^{-8}$; $Hg^{\cdot\cdot}$, 10^{-13}; HgI_4'', 2×10^{-14}. The **transport numbers** have been studied by H. N. Morse, and E. Rieger.

The electrical conductivity of soln. of mercuric iodide in liquid ammonia have been measured by H. P. Cady; in alcohol and in ether by W. Hampe, and by C. Cattaneo; in liquid methylamine by H. D. Gibbs, and by F. F. Fitzgerald; in pyridine, by A. Sachanoff, and A. T. Lincoln; in allyl mustard oil, by J. H. Mathews; in methyl acetate, by H. Steiner; and in acetic anhydride, acetone, epichlorhydrin, methyl alcohol, ethyl acetate, acetyl chloride, salicylaldehyde, aniline, dimethyl sulphate, and benzonitrile by L. I. Shaw.

M. Saladin[11] found the **solubility** of mercuric iodide in water to be very small, and H. Arctowsky noted that the solubility increased considerably with a rise of temp. The aq. soln. are more or less hydrolyzed, and H. Arctowsky noted the formation of a mercuric oxyiodide at 170°. The brownish six-sided rhombohedral crystals obtained by M. Saladin by the spontaneous evaporation of the aq. soln. are probably an oxyiodide. E. Bourgoin says that at 17·5° a litre of water dissolves 0·0403 grm. of the iodide; and at 22°, 0·0536 grm. P. Rohland obtained a similar result. H. N. Morse found a solubility of 0·06 grm. per litre at 25°. F. Kohlrausch and F. Rose reported much lower values, namely, 0·002 milligram eq. or 0·0004 grm. per litre at 18°; and later F. Kohlrausch gave 0·0002 to 0·0004 mgrm.; M. S. Sherrill, R. Abegg, and G. Bodländer have also made estimates of the solubility of mercuric iodide in water. The discordant data correspond with A. C. Dunningham's statement that the solubility of mercuric iodide in water is too small to estimate accurately. As previously indicated, both the red and yellow modifications form identically the same soln.

The solubility of mercuric iodide in *methyl alcohol* between 15° and 20° is given by P. Rohland as 3·24 grms. of salt per 100 grms. of alcohol and the sp. gr. of the soln. is 0·799. C. A. L. de Bruyn gives 3·16 grms. at 19·5°; and O. Sulc, 6·512 grms at 66°, the b.p. W. Herz and G. Anders found at 25° 10 c.c. of methyl alcohol dissolve 0·259 grm. of mercuric iodide, and that the solubility decreases as the

proportion of water increases, being 0·0445 grm. with 78·05 per cent. alcohol; 0·0158 grm. with 64 per cent. alcohol; and 0·0044 grm. with 47·06 per cent. alcohol. P. Rohland found 100 grms. of *ethyl alcohol* at 15° to 20° dissolve 1·42 grms. of mercuric iodide (sp. gr. of soln. 0·810); E. Bourgoin, 1·48 grms. at 18°; C. A. L. de Bruyn, 2·09 grms. at 19·5°; W. Herz and M. Knoch, 2·19 grms. at 25° (sp. gr. of soln. 0·803); and O. Sulc, 4·325 grms. at 78°, the b.p. O. Schönrock measured the sp. gr. of alcoholic soln. The solubility is diminished with increasing proportions of water, thus, at 25°, W. Herz and M. Knoch found 100 c.c. of a soln. of 95·82 per cent. alcohol have 1·162 grms. of mercuric iodide; 86·74 per cent. alcohol, 0·623 grm.; and 67·63 per cent. alcohol, 0·204 grm. The sp. gr. of the three last-named soln. are 0·80950, 0·82996, and 0·87214 respectively. W. Herz and F. Kuhn have measured the solubility of mercuric iodide in mixtures of methyl and ethyl alcohols. P. Rohland found 100 grms. of *propyl alcohol* dissolve 0·826 grm. of mercuric iodide between 15° and 20°, and the soln. has a sp. gr. 0·816. W. Herz and F. Kuhn have measured the solubility of mercuric iodide in mixtures of propyl alcohol with ethyl and with methyl alcohols. S. von Laszcynsky found that 100 grms. of *amyl alcohol* at 13° dissolve 0·66 grm. of mercuric iodide; at 71°, 3·66 grms.; at 100°, 5·30 grms.; and at 133·5°, 9·57 grms. O. Sulc found 100 grms. of *isopropyl alcohol* at its b.p., 81°, dissolve 2·266 grms. of mercuric iodide; and *isobutyl alcohol* likewise at its b.p., 105°–107°, 2·433 grms. J. H. Kastle and M. E. Clark say that mercuric iodide is more soluble in *allyl alcohol* than in ethyl alcohol. N. A. Orloff and M. Adams have studied the reactions of mercuric iodide in alcoholic soln.

M. Saladin noted in 1831 the low solubility of mercuric iodide in *ether*; according to S. von Laszcynsky, 100 grms. of ether dissolve 0·62 grm. of the iodide at 0°, 0·97 grm. at 36°, and, according to O. Sulc, 0·47 grm. at 35°, the b.p. of ether. S. G. Liversedge, and M. François used the fact for extracting mercuric iodide from certain mixtures in analytical work. S. von Laszcynsky found the solubility of mercuric iodide in 100 grms. of *acetone* to be 2·83 grms. at −1°; 3·36 grms. at 18°; 4·73 grms. at 40°; and 6·07 grms. at 58°. W. H. Krug and K. P. McElroy give 2·09 grms. at 25°, and O. Sulc gives 3·249 grms. at 56°, the b.p. W. Reinders gives a solubility of 1·95 per cent. for the red and 3·00 per cent. for the yellow iodide at 25°, but it is probable that equilibrium was not attained with the red salt. D. Gernez and L. Levi Bianchini have studied the reactions of mercuric iodide in acetone soln. D. Gernez found mercuric iodide to be soluble in *acetaldehyde*, W. Reinders in *benzaldehyde*, and L. I. Shaw in *salicylaldehyde*. According to O. Sulc, 100 grms. of *chloroform* dissolve 0·040 grm. of the iodide at 18°–20°, and 0·163 grm. at 61°, the b.p.; *bromoform*, 0·486 grm. at 18°–20°; *carbon tetrachloride*, 0·006 grm. at 18°–20°, and 0·094 at 75°, the b.p.; *ethyl bromide*, 0·643 grm. at 18°–20°, and 0·773 grm. at 38°, the b.p.; *ethylene dibromide*, 0·748 grm. at 18°–20°; H. Gautier and G. Charpy give 0·553 grm. at 15°. O. Sulc further found that 100 grms. of *ethyl iodide* dissolve 2·041 grms. of mercuric iodide at 18°–20°; *ethylene dichloride*, 1·200 grms. at 8·55°, the b.p.; *isobutyl chloride*, 0·328 grm. at 69°. J. H. Kastle and M. E. Clark found mercuric iodide to be soluble in *ethyl bromide*, *propyl bromide*, and *butyl bromide*. W. Reinders also found it to be soluble in *amyl bromide*, *amyl iodide*, *benzyl iodide*, and *naphthyl bromide*. O. Sulc found 100 grms. of *methyl formate* dissolve 1·166 grms. at 36°–38°; *ethyl formate*, 2·150 grms. at 52°–55°; *methyl acetate*, 2·500 grms. at 56°–59°; J. Schröder and H. Steiner also found 2·3 grms. were dissolved at the b.p. of this solvent, and F. Bezold, 1·1 grms. at 18°. According to E. Alexander, mercuric iodide is slightly soluble in *ethyl acetate*; M. Hamers found 100 grms. of the anhydrous solvent at 18° dissolve 1·470 grms. or 0·0033 mols of the iodide, and that the solubility increases with rise of temp. W. Herz and G. Anders measured the solubility of mercuric iodide in mixtures of *ethyl acetate* and water. J. H. Kastle and M. E. Clark found mercuric iodide to be very soluble in *ethyl propionate*, *ethyl butyrate*, *ethyl isobutyrate*, *ethyl salicylate*, and *phenyl salicylate*. W. Reinders found mercuric iodide to be soluble in *amyl acetate*. S. von Laszcynsky found 100 grms. of ethyl acetate dissolved 1·49 grms. of mercuric iodide at −20°; 1·56 grms. at 17·5°; 1·64 grms. at 21°; 2·53 grms. at 40°; 3·19 grms. at 55°; 4·31 grms. at 76°; and O. Sulc says 4·20 grms. at the b.p. 74°–78°. W. Reinders says that *diethyl oxalate* at its b.p. dissolves 12·5 per cent. of mercuric iodide, and 2·5 per cent. at 100°. F. Bezold and M. Hamers have studied the chemical reactions of mercuric iodide in soln. of ethyl acetate. O. Sulc found 100 grms. of *acetal* dissolve 2·000 grms. of mercuric iodide at 105°; *epichlorhydrin*, 6·113 grms. at 117°; and *hexane*, 0·072 grm. at 67°. J. W. Retgers found 100 grms. of *methylene iodide* dissolved 2·5 grms. of the iodide at 15°, 16·6 grms. at 100°, and 58·0 grms. at 180°. S. von Laszcynsky also gives for 100 grms. of *benzene*, 0·22 grm. at 15°; 0·88 grm.

at 60° ; 0·95 grm. at 65° ; 1·24 grms. at 84° ; O. Sulc gives 0·825 grm. at the b.p., 80° ; and H. Gautier and G. Charpy, 0·217 grm. at 15°. C. Melm and A. P. N. Franchimont also studied the solubility of mercuric iodide in *benzene*, and M. S. Sherrill, the partition coeff. of this salt between water and benzene. J. H. Kastle and M. E. Clark say mercuric iodide is more soluble in *toluene* than in alcohol. W. Reinders found mercuric iodide to be soluble in *acetic acid*, M. Rosenfeld in *acetic anhydride*, and G. C. Wittstein in soln. of *ammonium succinate*. A. Werner says that mercuric iodide is sparingly soluble in *methyl sulphide* and *ethyl sulphide*, and that there is some decomposition, gas is evolved, and addition products are formed. J. H. Mathews also says mercuric iodide is soluble in *allyl mustard oil*. A. Werner found ethyl sulphide forms addition products. F. F. Fitzgerald, and H. D. Gibbs said that mercuric iodide is very soluble in *methylamine* ; H. Vohl, in *aniline*. According to M. François, mercuric iodide in aniline soln. is reduced to mercury when the soln. contains more than 26 grms. of mercuric iodide to 100 grms. of aniline. J. H. Kastle and M. E. Clark said that mercuric iodide is soluble in *naphthalene*, in *ψ-cumene*, *ethyl cyanide*, *phenyl cyanide* ; L. Mascarelli, in *nitrobenzene*, *nitrotoluene*, and *nitronaphthalene* ; and A. Werner, in *benzonitrile* and other aromatic nitriles. A. Naumann said that at 18°, 100 grms. of benzonitrile dissolve 0·98 grm. of mercuric iodide, and that the solubility is much greater if potassium iodide be present. W. Eidmann found mercuric iodide to be soluble in *methylal*. M. François found mercuric iodide to be very soluble in *phenol*, for 100 grms. of boiling phenol dissolve 110 grms. of mercuric iodide ; C. Méhu gave 2·0 grms. per 100 grms. of solvent at 100°. J. Schröder and A. Naumann also found mercuric iodide to be soluble in *pyridine* ; W. Reinders in *toluidine* ; and D. Gernez in *quinoline*. O. Schönrock measured the sp. gr. of pyridine soln. J. Schröder has studied the chemical reactions of mercuric iodide in soln. of pyridine. A. Werner found the *piperidine* reduces mercuric iodide to the metal, the reaction is instantaneous at 100°. C. Méhu found that 100 grms. of *bitter almond oil* dissolved 0·5 grm. of mercuric iodide at 25°, and 1·3 grms. at 100° ; *castor oil*, 4·0 grms. at 25°, 20·0 grms. at 100° ; *nut oil*, 1·3 grms. at 100° ; *vaseline*, 0·025 grm. at 25°, 0·20 grm. at 100° ; *poppy oil*, 1·0 grm. at 25° ; and *olive oil*, 0·4 grm. at 25°. W. Reinders also noted the solubility of mercuric iodide in *turpentine* and *petroleum*. M. C. Lea found mercuric iodide dissolves readily in hot *glycerol*, forming a colourless soln., and T. Fairley said that 100 parts of glycerol dissolve 0·294 part of the salt.

According to P. Walden,[12] mercuric iodide is soluble in *sulphur chloride*, S_2Cl_2, forming a reddish-brown soln. ; in *thionyl chloride*, $SOCl_2$, forming a reddish-yellow soln. ; in *sulphuryl chloride*, SO_2Cl_2, forming a yellow soln. ; in *phosphoryl chloride*, $POCl_3$, forming a colourless soln. ; in *phosphorus tribromide*, PBr_3, forming a yellowish coloured soln. ; and in *arsenic trichloride*, $AsCl_3$, and in *arsenic tribromide*, $AsBr_3$, forming colourless soln. E. H. Büchner finds mercuric chloride to be insoluble in liquid *carbon dioxide*. According to P. Walden and M. Centnerszwer, mercuric iodide is soluble in liquid *sulphur dioxide*. The sat. soln. at the critical temp., 158·2°, contains 0·7 per cent. of mercuric iodide, and the critical temp. of the soln. increases with increasing conc. P. Niggli said that liquid sulphur dioxide in a sealed tube at 254° contains 6·2 per cent. of mercuric iodide in soln. The presence of potassium or rubidium iodide, or of mercuric bromide augments the solubility of mercuric iodide. C. E. Linebarger, H. Arctowsky, and H. Gautier and G. Charpy have measured the solubility of mercuric iodide in *carbon disulphide*. The percentage solubility, S, is

	−116°	−86·5°	−10°	0°	5°	10°	15°	20°	25°	30°
S .	0·017	0·024	0·107	0·173	0·207	0·239	0·271	0·320	0·382	0·445

Mercuric iodide is **photosensitive** for R. Hunt,[13] and Lüppo Cramer showed that a film of this salt becomes brown on exposure to light ; and J. W. Slater found that blue light is particularly favourable in producing the change. O. Sulc observed that when a soln. of mercuric iodide in alcohol, chloroform, or ethyl bromide is exposed to light, free iodine and mercurous iodide are formed. The photosensitiveness of mercuric iodide in photographic emulsions has been studied by Lüppo Cramer, F. Kropf, A. P. H. Trivelli and S. E. Sheppard, etc. The results show that the emulsions are not so sensitive photochemically as those of the silver halides ; that the red emulsion is more sensitive than the yellow emulsion ; and that the yellow emulsion made at 80° is not so sensitive as the others. While mercuric and silver iodides are fairly sensitive, the double salt is only slightly so.

M. Berthelot [14] found that purified mercuric iodide is not decomposed if exposed

dry or moist in a sealed tube for a month to **sunlight,** and the decomposition often observed with pharmaceutical preparations is due to the reducing action of organic compounds. M. C. Lea noted that mercuric iodide is darkened and even blackened by the application of a high *pressure* without the liberation of iodine, for none could be extracted by alcohol. F. C. Phillips sublimed mercuric iodide in a stream of **hydrogen** without reduction; and H. Schulze calcined it in **oxygen** without decomposition. M. Kohn and A. Ostersetzer found that mercuric halides are reduced by **hydrogen peroxide** in alkaline soln., or by **sodium peroxide** with the liberation of mercury, and the reaction has been applied in quantitative analysis.

C. F. Rammelsberg obtained what he regarded as **tetramercuric trioxyiodide,** $HgI_2.3HgO$, by melting together mol. proportions of the two components; and he, as well as T. Weyl, obtained a similar product by the action of a dil. soln. of potassium hydroxide on mercuric oxide. A. Oppenheim also obtained a similar product by the crystallization of allylmercuric iodide from acetone. The yellow product is decomposed by drying at 100°, and when exposed to the action of dry ammonia. P. Yvon also obtained a pale yellow sublimate—approximately $7HgI_2.6HgO$—by rapidly heating mercurous iodide. The mixture decomposes on exposure to light, and turns red. H. Moissan noted that **fluorine** attacks mercuric iodide in the cold, the reaction is accompanied by *une flamme très vive*, and the formation of a yellow compound—mercuric fluoride or iodofluoride. Molten **ammonium fluoride** was found by C. Poulenc not to attack mercuric iodide. E. Filhol noted that if **chlorine** be passed through water in which mercuric iodide is suspended, mercuric chloride and iodine trichloride are formed. According to M. Berthelot, the displacement of iodine by chlorine develops 14·3 Cals. with red mercuric iodide, and 17·3 Cals. with the yellow salt. P. Hautefeuille found that mercuric iodide is not decomposed when heated in a stream of **hydrogen chloride;** J. J. Colin, P. F. G. Boullay, H. Saha and K. N. Choudhuri noted that the salt is soluble in **hydriodic acid,** and also in **hydrochloric acid,** and, according to H. Köhler, conc. hydrochloric acid is one of the best agents for crystallizing mercuric iodide since the hot acid dissolves a considerable amount of the salt without decomposition. C. F. Rammelsberg found that mercuric iodide dissolves in a soln. of **bleaching powder,** and when the soln. is heated a gelatinous mass of basic calcium periodate is deposited and mercuric chloride remains in soln. J. W. Clark noted that a soln. of mercuric iodide dissolves mercurous iodide and iodine. J. H. Kastle and M. E. Clark found that **cyanogen iodide,** CyI, decomposes mercuric iodide in suspension in water, forming mercuric cyanide and iodine.

J. Timmermanns found that soln. of mercuric iodide in iodine give high values for the mol. wt. F. Olivari said that this is not to be attributed to the formation of **mercuric polyiodides** since the f.p. curve of mixtures of mercuric iodide and iodine shows no signs of their formation. The curve has a eutectic at 101·4° with 12·5 molecular per cent. of mercuric iodide. S. Schlesinger obtained a white powder by the action of hot fuming nitric acid on mercuric iodide; this product, once thought to be *mercuric periodide*, HgI_3, was shown by S. M. Jörgensen to be mercuric iodate. R. Hunt also obtained a purplish-brown product—with 27·9 per cent. of mercury and 72·1 per cent. of iodine—very nearly corresponding with HgI_4, by the action of a soln. of potassium iodide sat. with iodine upon an aq. soln. of mercuric chloride. There is nothing to show that the product is a homogeneous or chemical individual. S. M. Jörgensen treated a hot (50°) alcoholic soln. of potassium triiodide with an excess of a cold aq. soln. of mercuric chloride, and obtained a brown crystalline precipitate which was rapidly washed with cold water. It could not be dried without decomposition. The product is thought to be a mixture of **mercuric hexaiodide,** HgI_6, with some red and yellow mercuric iodides. The brown crystals belong to the rhombic system, and in form resemble yellow mercuric iodide; they are slowly decomposed by cold water; they gradually lose iodine on exposure to air; they are reduced by zinc and cold water, forming zinc iodide and zinc amalgam; and they are decomposed by alcohol, forming red mercuric iodide. W. Herz and

W. Paul measured the solubility of iodine in mercuric chloride soln., and partition experiments with carbon tetrachloride indicate the existence of **mercuric dibromo-iodide,** $HgBr_2I_2$, and of **mercuric dichloroiodide,** $HgCl_2I_2$.

Mercuric iodide is not attacked by **sulphuric acid** in the cold, but when heated, the salt is decomposed; A. Ditte did not obtain salts analogous with $HgSO_4.2HBr$ and $HgSO_4.2HCl$ as is the case when sulphuric acid reacts with the corresponding mercuric halides. K. Barth found that although mercuric iodide dissolves in soln. of the **alkali sulphites,** he could not obtain double salts analogous with those obtained with mercuric chloride or bromide. F. Field and E. Meusel found mercuric iodide dissolves in a soln. of **sodium thiosulphate,** and when the colourless liquid is heated, it deposits red mercuric sulphide; J. M. Eder and G. Ulm say that two mols are required for dissolving one of mercuric iodide, and C. F. Rammelsberg supposes that a double salt is formed.

The solvent action of liquid **ammonia,** and the formation of ammonia compounds of mercuric iodide are discussed in a special section. K. A. Hofmann and E. C. Marburg prepared **mercuric hydrazine-iodide,** $HgI_2.N_2H_4$, by adding an excess of hydrazine hydrate to an alcoholic soln. of mercuric iodide. The resulting yellow needle-like crystals are more stable than the corresponding bromide or chloride. They are decomposed by exposure to light, and by treatment with water. S. Schlesinger found mercuric iodide to be soluble in **nitric acid;** according to K. Kraut, when nitric acid of sp. gr. 1·5 is boiled with mercuric iodide, mercuric iodate, $Hg(IO_3)_2$, is formed, and a similar result is obtained with an acid of sp. gr. 1·4, but a small quantity of mercuric nitrate then passes into soln.; with an acid of sp. gr. 1·3, white micaceous plates of **mercuric nitratoiodide,** $HgI_2.Hg(NO_3)_2$, separate out on cooling; and finally, with an acid of sp. gr. 1·2, red crystals of unchanged mercuric iodide accompanied by white scales of the nitrato-iodide separate out on cooling. According to F. Venturoli, alcoholic soln. of **phosphorus** and mercuric iodide give a compound, **mercuric phosphoiodide,** Hg_2PI_3, or $PI(HgI)_2$, presumably: $8HgI_2+6P=2PI(HgI)_2+P_2I_4$; and when heated, $PI(HgI)_2=HgI_2+HgI+P$, some phosphoric and phosphorous acids, hydriodic acid, and ethyl iodide are simultaneously formed. J. B. Berthemot found that **antimony** or **bismuth** when heated with mercuric iodide and water furnishes bismuth oxyiodide in the one case, and antimonic oxide in the other. K. Haack states that mercuric iodide is not affected by boiling with soln. of **sodium hydrogen phosphate or arsenate,** or by fusion with either of these salts. M. Kohn found arsenious oxide in alkaline soln. reduces mercuric iodide. According to B. E. Howard, when treated with **hypophosphorous acid,** hydriodic acid is produced in which mercurous iodide is dissolved, and the reduction is incomplete.

J. B. Berthemot studied the action of various metals on mercuric iodide; he found that many of the heavy metals, alone or with water, withdraw all or half the iodine from mercuric iodide, and that the resulting metal iodide may or may not unite with part of the mercury iodide to form double salts, iodo-mercuriates. When heated and triturated with mercuric iodide and water, **zinc** forms zinc iodide and zinc amalgam with the evolution of much heat; **cadmium** behaves similarly; **tin** decomposes slowly, and with half an hour's boiling, **tin** amalgam and stannic oxide are formed, but undecomposed mercuric iodide and stannic iodide are still present; **iron** forms mercurous iodide, and afterwards, if heat be applied, mercury and ferrous iodide are formed; **copper** gives a similar result; **lead** forms lead iodide and mercurous iodide; and **silver** behaves similarly. C. F. Rammelsberg rubbed up mercuric iodide with **potassium** and formed potassium iodide and mercury; the reaction is attended by the evolution of much heat. T. Fischer also noticed the decomposition of mercuric iodide, suspended in water by **magnesium** powder.

J. B. Berthemot found that mercuric iodide is decomposed by soln. of the alkali hydroxides, forming mercuric oxide and a soln. of a double iodide of mercury and the alkali metal; if the soln. of the alkali hydroxide be very dil., C. F. Rammelsberg says that mercuric oxyiodide separates out. J. B. Berthemot also says that when

mercuric iodide is boiled with a soln. of **potassium hydroxide,** mercuric oxide separates out, and a yellow soln. of a double salt of mercuric and potassium iodide is formed, which on cooling deposits crystals of mercuric iodide, and then greenish-yellow needles of potassium iodomercuriate. An alcoholic soln. of potassium hydroxide acts similarly, but more readily. Soln. of **sodium, barium,** and **strontium hydroxides** act similarly; so does an alcoholic soln. of **calcium hydroxide** in alcoholic but not in aq. soln. **Magnesium or aluminium hydroxides** have no action; similarly also with **magnesium carbonate.** Aq. soln. of **sodium or potassium carbonate** do not decompose mercuric iodide, but alcoholic soln. do so. Mercuric iodide is soluble in soln. of many of the normal salts. R. H. Brett found it to be soluble in soln. of **ammonium nitrate.** Mercuric iodide dissolves in soln. of **mercuric chloride, acetate, or nitrate,** and, according to H. Morse, a litre of N-$Hg(NO_3)_2$ dissolves 48·0 grms. of mercuric iodide. M. François observed a reversible reaction between mercurous nitrate and mercuric iodide: $HgI_2+2HgNO_3 \rightleftharpoons Hg(NO_3)_2+2HgI$. G. C. Wittstein noted the ready solubility of mercuric iodide in a hot soln. of **ammonium sulphate** and **ammonium carbonate;** G. C. Wittstein, and H. Saha and K. N. Choudhuri, and R. Böttger in a cold soln. of **ammonium chloride;** P. F. G. Boullay, and M. C. Lea, in soln. of **potassium chloride, sodium chloride, calcium chloride,** and **barium chloride.** H. Grossmann found mercuric iodide to be very soluble in soln. of **ammonium bromide,** and F. Jander in soln. of **potassium iodide, potassium bromide,** and **ammonium iodide,** with the formation of complex salts—*e.g.* NH_4HgI_3. P. Harth could find no signs of a reaction with potassium chloride or bromide when the soln. is extracted with ether. A soln. of mercuric iodide in potassium iodide was used by E. Sonstadt and A. von Lasaulx as a heavy liquid—*Sonstadt's heavy liquid*—for the separation of minerals of different sp. gr. M. François found that with **ammonium iodide** a balanced reaction: $NH_4I+HgI_2 \rightleftharpoons NH_4HgI_3$, is established. J. Philipp has studied the solubility of mercuric iodide in soln. of **potassium thiocyanate,** and isolated a double salt: $HgI_2.2KSCy.2H_2O$. Mercuric iodide is also soluble in soln. of **potassium cyanide;** according to P. Harth, two mols of potassium cyanide completely decompose a mol of mercuric iodide into mercuric cyanide and potassium iodide as proved by extraction with ether. F. Labouré noted that when mercuric iodide is treated with a soln. of **stannic chloride,** it is decomposed with the loss of iodine, becoming yellowish-red, yellow, greenish-yellow, green mercurous iodide, and finally into a mixture of mercury and stannic iodide. Mercuric iodide forms a number of double salts with other metal chlorides, and also with a number of organic bases.[15] A mixture of mercuric iodide with 96 per cent. of benzoated lard or suet is the *unguentum hydrargyri iodidi rubri* of the pharmacopœia which is used as an ointment in some skin diseases. A mixed soln. of equal parts of arsenious and mercuric iodides is the *liquor arsenii et hydrargyri iodidi*, or *Donovan's solution* of the pharmacopœia.

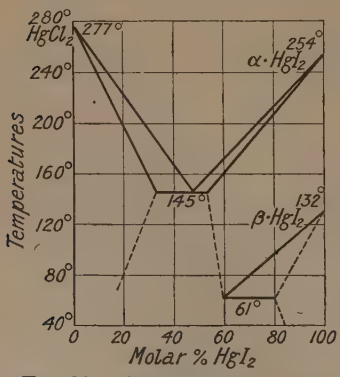

FIG. 29.—Freezing-point Curves of Mixtures of Mercuric Iodide and Chloride.

H. Moissan[16] suggested the bare possibility of *mercuric fluoriodide* being formed by the action of fluorine on mercuric iodide. According to J. S. van Nest, H. Köhler, and W. C. Luczizky, only a limited series of mixed crystals is formed between mercuric chloride and iodide. M. Padoa and C. Tibaldi's fusion curves, Fig. 29, show that α-mercuric iodide and mercuric bromide give a typical V-eutectic. The same diagram shows the effect of mercuric chloride on the transition point of mercuric iodide. The regions of mixed crystals are also indicated in the diagram. There are no signs of the formation of any mixed salts under these conditions. M. Berthelot found the heat of combination of the two salts is

almost zero. J. von Liebig prepared what has been considered to be *mercuric tetrachlorodi-iodide*, $2HgCl_2.HgI_2$, by crystallization during the cooling of a boiling aq. soln. of mercuric chloride sat. with the iodide; F. Selmi, and E. Riegel, likewise by boiling mercuric chloride and water with an excess of iodine. H. Köhler showed that the products are not chemical individuals. According to J. L. Lassaigne, a soln. of mercuric chloride sat. in the cold with mercuric iodide furnishes colourless needles with $HgCl_2 : HgI_2$ in the molar proportions 40 : 1; an aq. or alcoholic soln. of iodine nearly decolorized with mercuric chloride, deposits on evaporation a similar product. If the iodide be in excess the crystals appear red owing to the presence of mercuric iodide which may be removed by re-crystallization from water. The aq. soln. has the general reactions of mercuric chloride; it gives no blue coloration with starch even when chlorine or sulphur dioxide has been added. A soln. of mercuric chloride decolorizes blue iodide of starch, due, said N. A. E. Millon, to the formation of mercuric iodide and iodine chloride; the blue colour appears if potassium iodide is added, because the iodine chloride is decomposed. P. F. G. Boullay and A. Larocque prepared what has been regarded as *mercuric chloroiodide*, HgClI, or $HgI_2.HgCl_2$, as a yellow powder, by cooling a soln. of mercuric chloride sat. with the iodide. The product soon changes to a red colour; if the soln. of mercuric chloride be incompletely sat. with the iodide, it first deposits a yellow powder, then yellow crystals, which soon turn red. H. Köhler confirmed the preceding results, and said the best yield is obtained by heating 4·5 grms. of mercuric chloride with 2·5 grms. of iodine in a sealed tube at 140°–160°, or by heating 4·5 grms. of mercuric iodide and 2·7 grms. of mercuric chloride with a little water in a sealed tube for 4–5 hrs. at 140°–160°; and M. Berthelot and S. de Luca, by allowing conc. hydrochloric acid to act on mercury in the presence of allyl iodide. The yellow form of this compound is in rhombic crystals, the red form in tetragonal prisms. According to H. Köhler, mercuric chloroiodide becomes citron-yellow at 125°, and melts at 153° to a golden-yellow liquid. It boils at 315°, and sublimes unchanged at a somewhat lower temp. It is very sparingly soluble in water, but rather soluble in hot alcohol. By chlorine it is converted into mercuric chloride with development of heat; it may be sublimed in a current of hydrochloric acid, sulphur dioxide, or hydrogen sulphide without decomposition, but in dry ammonia it falls to a grey powder. It is somewhat soluble in dil. hydrochloric acid, and from this soln. hydrogen sulphide does not precipitate black mercuric sulphide even when hot, but a voluminous greenish-yellow precipitate of mercuric chloroiodosulphide, Hg_2SClI, which is sensitive to light. An aq. soln. of mercuric chloroiodide is used as A. von Hübl's reagent for measuring the iodine number of fats. P. Welmans preferred a soln. in ethyl acetate. C. Böttinger found it gives yellow products when added to gallic acid or tannin soln. W. Reinders,[17] W. C. Luczizky, J. S. van Nest found that fused mixtures of mercuric bromide and iodide, or crystals obtained from the aq. soln. furnishes a complete series of mixed crystals—*vide* Figs. 29 and 30. K. Beck measured the viscosity of the mixtures; and P. Niggli, the f.p. and sp. gr. M. Berthelot found that the heat of union of mercuric iodide and bromide is almost zero. The m.p. of mixed crystals with more than 25 per cent. of mercuric bromide was found by P. Niggli to be lowered by sulphur dioxide. The alleged *mercuric bromoiodide*, HgIBr, obtained by A. Oppenheim by the action of alkyl iodides on an acetone soln. of mercuric bromide, or by crystallization from ether or acetone soln. of the component salts, thus appears as one member of an unbroken series of mixed crystals. H. Grossmann prepared rhombic plates of **ammonium mercuric tribromotetraiodide,** $3NH_4Br.2HgI_2$, by saturating a cold conc. soln. of ammonium bromide with mercuric iodide, evaporating over sulphuric acid, and removing the crystals of ammonium bromide; the crystals

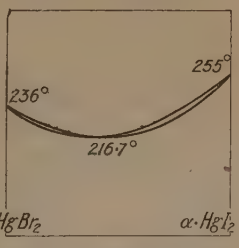

FIG. 30.—Fusion Curve of Mixtures of Mercuric Bromide and Iodide.

are dichroïc, being yellow when viewed parallel and pale yellow when viewed perpendicular to the prism edges. The crystals are decomposed by water; he also obtained similar crystals of **ammonium mercuric dibromodiiodide,** $2NH_4Br.HgI_2$, by concentrating on the water-bath a soln. of a mol of mercuric iodide in a conc. soln. of 2 mols of ammonium bromide.

According to R. Abegg and G. Bodländer's hypothesis of electro-affinity, the tendency of the mercuric halides to form complex cations is weaker the stronger the anion, combining with the mercuric ion to form the cation, since an increase in the electro-affinity of the halogen radicle should be accompanied by an increase in the tendency of the radicle to ionize according to the scheme $HgX' \rightarrow Hg'' + X'$. V. Borelli has shown that this is the case with the complex salts formed by mercuric perchlorate with mercuric iodide, bromide, chloride, cyanide, and thiocyanide. Here the tendency to form complex ions is greatest with mercuric iodide and cyanide, less marked with the bromide, and so slight with the chloride that the double salt cannot be isolated. **Mercuric perchloratoiodide,** $I.HgClO_4$, forms bundles or mammillary masses of white, opaque prisms which deliquesce and turn yellow in air, and are decomposed by water with the liberation of mercuric iodide. The lowering of the f.p. in water gives values for the mol. wt. less than that calculated for the complete ionization and for the partial hydrolysis of the perchlorate: $Hg(ClO_4)_2 + H_2O = HClO_4 + Hg(OH)ClO_4$, studied by H. Ley and C. Heimbucher. The depression of the f.p. of water by mercuric perchlorate is diminished by mercuric iodide, and this the more the greater the proportion of iodide present in the soln. Accordingly, the molar conc. of the complex undergoes a corresponding decrease. The lowering of the conductivity of mercuric perchlorate soln. by addition of potassium iodide is due to a decrease in the conc. of the ions, and to the lower mobility of the new ions. The addition of mercuric iodide produces an increase in the molar conc. of mercuric perchlorate soln. when this is not excessively conc., and a decrease when an excess of the perchlorate is present. V. Borelli attributed these results to various reactions between mercuric iodide and the ions Hg'' and ClO'_4 originally present in the soln. Mercuric iodide probably unites with the Hg''-ions to give complex cations, a view in harmony with measurements of the transport numbers of soln. of mercuric iodide containing an excess of the perchlorate.

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§ 25. Ammino-, Ammino-basic, and Aquo-amminobasic Salts of Mercuric Iodide

According to G. Gore,[1] E. C. Franklin and C. A. Kraus, and H. P. Cady, mercuric iodide is soluble in liquid ammonia. According to E. C. Franklin, the soln. in liquid ammonia suffers amminolysis, $2HgI_2+4NH_3 \rightleftharpoons Hg:N.HgI+3NH_4I$, and M. François represents the hydrolysis with conc. aqua ammonia as occurring in two stages, $HgI_2.2NH_3 \rightleftharpoons NH_2HgI+NH_4I$, and $2NH_2HgI \rightleftharpoons Hg:N.HgI+NH_4I$; if dil. aqua

ammonia be used, a compound $Hg_9N_4I_6$ is formed. According to R. Böttger, when aq. ammonia acts on mercuric iodide, a brown powder—probably $NH_2Hg.O.HgI$ or $NHg_2I.H_2O$—is formed along with a yellow liquid; G. C. Wittstein says that aq. ammonia turns mercuric iodide white, and later, when heated, it forms brownish-red powder—probably $NH_2Hg.O.HgI$. According to F. M. G. Johnson and N. T. M. Wilsmore, the soln. of mercuric iodide in aqua ammonia, sp. gr. 0·880, does not freeze at the m.p. of liquid ammonia. A. Cailliot and M. Corriol found that when the soln. obtained by treating mercuric iodide with aq. ammonia is evaporated in air, white needle-like crystals of **mercuric monamminoiodide,** $HgI_2.NH_3$, are formed. C. F. Rammelsberg supposed it to be $HgI_2(NH_3)_2HgI_2$; and L. Pesci, $8NH_4I.4HgI_2.3NHg_2I$. C. F. Rammelsberg says that a similar product is formed by allowing aq. ammonia to act upon mercuric iodide until a white powder is formed, and J. Nessler added that if conc. aq. ammonia be used, the diammino-compound is formed. C. F. Rammelsberg made the monammino-compound by precipitation from a soln. of mercuric iodide in an alkali thioantimonate by the addition of aq. ammonia; and J. Nessler obtained it by treating a soln. of a mol of mercuric iodide and two of potassium iodide with aqua ammonia; if an excess of ammonia be used, the diammino-compound is formed. The monammino-salt loses its ammonia rapidly in air and still more rapidly under water or dil. acids—mercuric iodide remains.

According to H. Rose, 100 parts of mercuric iodide absorb 7·01 parts of ammonia, forming **mercuric diamminoiodide,** $HgI_2.2NH_3$; the dirty white product loses its ammonia in a few hours on exposure to air and reforms red mercuric iodide. W. Peters, H. Ley and G. Wiegner also found that by exposing mercuric iodide to the action of ammonia gas in a eudiometer two mols are absorbed, and that the absorbed gas is given off in vacuo. M. François, and A. Colson also made the same compound by the action of dry ammonia on dry red mercuric iodide; A. Colson made it by passing dry ammonia through a soln. of mercuric iodide in dry benzene; L. Pesci, by adding aqua ammonia sat. at 0° to a soln. of mercuric iodide in potassium or ammonium iodide; P. Lemoult, by saturating a soln. of potassium tetraiodomercuriate, K_2HgI_4, with conc. aqua ammonia and cooling to 0°; J. Nessler, by treating the monoammino-compound with conc. aqua ammonia, or ammonia gas; and J. Nessler, H. Saha and K. N. Choudhuri, by the action of a cold sat. soln. of ammonia on mercuric iodide, or, according to M. François, on mercurous iodide.

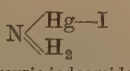
C. F. Rammelsberg represented this compound by the formula $(NH_3)_2HgI_2$, and T. Weyl, by $2NH_4I.NHg_2I$. It forms a colourless or pale yellow powder or needle-like crystals which are very unstable, so that when removed from the mother liquor, the crystals soon redden owing to the loss of ammonia and the formation of red mercuric iodide; according to H. Saha and K. N. Choudhuri, the crystals are stable in an atm. of ammonia. According to M. François, the dissociation takes place in two stages: **mercuric tetramminohexaiodide,** $3HgI_2.4NH_3$, is first formed: $3HgI_2(NH_3)_2 \rightleftharpoons 3HgI_2(NH_3)_4 + 2NH_3$; and the product then decomposes: $3HgI_2(NH_3)_4 \rightleftharpoons 3HgI_2 + 4NH_3$. The dissociation pressures are:

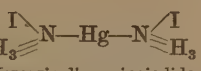
	$3HgI_2(NH_3)_2 \rightarrow 3HgI_2.4NH_3 + 2NH_3$				$3HgI_2.4NH_3 \rightarrow 3HgI_2 + 4NH_3$			
Temp.	0°	25°	55°	80°	15°	25°	55°	95°
Press. mm.	8	37	219	732	1	2	12	107

Mercuric diamminoiodide is decomposed completely by water, and mercuric iodide is formed. M. François says the diammino-compound is insoluble in a little ammonia but soluble in a large quantity. Aq. ammonia forms first a yellow soln. which turns brown, and, according to J. Nessler, deposits brown $NH_2Hg.O.HgI$; and, according to L. Pesci, if small portions are added to a large excess of ammonia, NHg_2I is formed. M. François says that with conc. ammonia, NHg_2I is formed, and that the reaction is reversible; and that with less ammonia NH_2HgI is formed by a reversible reaction. L. Pesci says that hydrogen sulphide converts mercuric diamminoiodide suspended in water into mercuric sulphide and a soln. of ammonium iodide; according to

M. François, ether dissolves the diammino-compound completely ; but, according to J. Nessler, ether dissolves it only partially, alcohol also dissolves it partially, forming a yellow or, with more alcohol, a brown mass. If the dil. ethereal soln. be added to a soln. containing free aluminate, or zincate, a yellow coloration is obtained—the presence of potassium cyanide, sulphide, or iodide hinders the coloration ; no coloration is obtained with alkali bicarbonate, potassium stannate, borax, or sodium phosphate. F. Ephraim and P. Mosimann made **mercuric zinc tetrammino-tetraiodide,** $[Zn(NH_3)_4]HgI_4$; **mercuric cadmium tetramminotetraiodide,** $[Cd(NH_3)_4]HgI_4.4H_2O$; and **mercuric cadmium hexamminotetraiodide,** $[Cd(NH_3)_6]HgI_4.6H_2O$.

M. François [2] prepared the iodine analogue of infusible white precipitate, **mercuric iodoamide,** NH_2HgI, by the action of conc. aqua ammonia added slowly and at long intervals on mercuric diamminoiodide, $Hg(NH_3)_2I$. The precipitate was dried in an atm. of ammonia. If large quantities of aqua ammonia are added at once, brown dimercuriammonium iodide, Hg_2NI, is formed. The reaction is reversible, $HgI_2.2NH_3 \rightleftharpoons NH_2HgI + NH_4I$, and with aq. ammonia of sp. gr. 0·923, at 21°, the conc. of the ammonium iodide, at equilibrium, was between 0·020-*N* and 0·023-*N*. Mercuric iodoamide forms a dirty white crystalline mass which is not reddened in air, and which is insoluble in ether. E. C. Franklin says that mercuric iodoamide may be also regarded as a basic mixture, $Hg(NH_2)_2.HgI_2$. M. François regards what has been called mercuric iodoamide, $NH_2.Hg.I$, as mono-mercuriammonium iodide, and he gives for the graphic formulæ of this compound and mercuric diamminoiodide, $Hg(NH_3)_2I_2$, and dimercuriammonium iodide, Hg : N.HgI,


Mercuric iodoamide.


Mercuric diamminoiodide.

Dimercuriammonium iodide.

As previously indicated, M. François found that if conc. aqua ammonia acts on mercuric diamminoiodide, or on mercuric iodide **dimercuriammonium iodide,** Hg_2NI, or Hg : N.HgI, is formed. M. François also prepared this compound by the action of alkali hydroxide on mercuric diamminoiodide.

Carefully stir 30 grms. of mercuric iodide in a glass mortar with 30 c.c. of aqua ammonia of sp. gr. 0·923, add 30 c.c. of ammonia, and stir the mixture 24 hrs. in a mortar with 90 c.c. of a 25 per cent. soln. of sodium hydroxide. Let the mixture stand under a bell jar with occasional stirring for five days. Draw off the liquid and again treat the solid with 90 c.c. of the 25 per cent. soda-lye, and heat the mixture for 2 hrs. on a water-bath. Wash by decantation with water, and dry at 50°.

T. Weyl first made it by the action of liquid ammonia on the basic iodide, $3HgO.HgI_2$, and dried the product in a stream of dry air, first at 100° and then at 130°, and he says that he was not successful in his attempts to make it from $(NHg_2)_2O$. E. C. Franklin also showed that this compound is formed by the amminolytic action of liquid ammonia on mercuric iodide, as well as by the action of potassium amide on an excess of mercuric iodide in soln. in liquid ammonia. The salt forms a dark red almost black crystalline powder or a dark brown powder which is very stable. It decomposes without explosion when heated in a tube—mercury and mercuric iodide sublime. It burns with a blue flame. It decomposes with the evolution of ammonia when boiled with a soln. of potassium hydroxide or chloride ; it is insoluble in water, but soluble in hydrochloric acid. Dil. hydrochloric acid converts it into a mixture of mercuric iodide and chloride, and ammonium chloride. It is soluble in aq. soln. of ammonium chloride. Mercuric diamminoiodide can be formulated as if it were a compound of ammonium and dimercuriammonium iodides, $3NH_4I.NHg_2I$.

A compound with the empirical composition Hg_2NH_2OI—the yellow precipitate formed by the action of J. Nessler's reagent on ammoniacal compounds—has been the subject of many investigations. E. C. Franklin regards it as **mercuric**

hydroxyiodoamine, HgOH.NH.HgI, *i.e.* the iodide of Millon's base; and it can be regarded as Hg(HgOH)NHI, graphically:

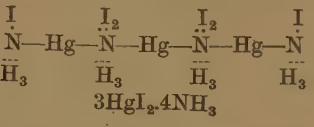
as *oxydimercuriammonium iodide*, $NH_2(Hg.O.Hg)I$, or as hydrated *dimercuriammonium iodide*, $Hg_2NI.H_2O$, but M. François could only prepare the anhydrous Hg_2NI.

According to E. C. Franklin, this compound is formed by the action of ammonia on mercuric iodide, and, in general, when mercuric iodide and ammonia are brought together in alkaline soln. For example, C. F. Rammelsberg, and T. Weyl made it by passing ammonia gas over $3HgO.HgI_2$ at 180°; C. F. Rammelsberg treated mercuric iodide with an excess of conc. aqua ammonia at 60°; the red iodide becomes white, brown, and finally reddish-brown: $4NH_3+2HgI_2+H_2O=3NH_4I+Hg_2NH_2OI$; the supernatant liquid is decanted off, and the solid is washed by heating it seven times with fresh aqua ammonia. J. Nessler washed the precipitate finally with ether. J. Nessler prepared the same product by treating an aq. soln. of potassium iodomercuriate with potassium hydroxide and ammonia; if a little alkali hydroxide be used the product is pale yellow and the colour darkens more and more as the amount of alkali is increased: $2K_2HgI_4+3KOH+NH_3=7KI+2H_2O+Hg_2NH_2OI$. L. Cramer obtained an emulsion by using soln. containing gum arabic or gelatine. C. F. Rammelsberg also converted the corresponding chloro-compound into the iodo-compound by digesting it with potassium iodide.

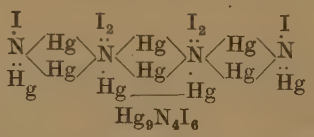
C. F. Rammelsberg reported that mercuric hydroxyiodoamide is a brown powder with a purple-red tinge. It loses a little hygroscopic moisture when heated to 128°, and when strongly heated in a retort, out of contact with air, it fuses to a brown liquid, which afterwards detonates with a blue light, and gives off mercury, mercuric iodide, ammonia, and nitrogen. When heated to 100° in a stream of hydrogen chloride, it appears dotted with yellow sparks, and emits white fumes; and if heated to the m.p., a sublimate is formed of mercuric amminoiodide, mercuric and ammonium chlorides, and ammonium iodide. The formation of water was not observed. According to H. B. Weiser, the iodide of Millon's base decomposes as low as 160°, but the reaction is not rapid until about 400°. The decomposing salt exhibits a luminescence more distinctly violet than the potassium flame. He added that the orange luminescence of mercury salts is due to the reaction $Hg^{\cdot}$-ions$\rightarrow$undissociated mercurous salts; the green luminescence to the reaction $Hg^{\cdot}$-ions$\rightarrow Hg^{\cdot\cdot}$-ions; and the violet luminescence to the reaction $Hg^{\cdot\cdot}\rightarrow Hg$. If heated with an aq. soln. of barium sulphide—or, according to J. Nessler, potassium sulphide—the contained nitrogen is all evolved in the form of ammonia; it dissolves in a warm aq. soln. of potassium iodide giving off ammonia—the liquid contains potassium iodomercuriate, K_2HgI_4, and free potassium hydroxide; mercuric hydroxyiodoamide, dissolves in hydrochloric acid, forming a colourless liquid which on cooling deposits crystals of mercuric iodide and mercuric chloroiodide; it is not decomposed by boiling potash-lye, and no ammonia is therefore given off under these conditions.

The compound **enneamercuriammonium iodide,** $Hg_9N_4I_6$, was made by M. François by the action of a $\frac{1}{10}N$-soln. of ammonia on mercuric tetramminohexaiodide, $3HgI_2.4NH_3$. The white mass becomes brown. After standing 8 hrs., the supernatant liquid is decanted off; the solid washed with water, and dried in air. It is then washed by decantation with ether. The reaction is reversible and is represented: $3Hg_3(NH_3)_4I_6+nNH_3\rightleftharpoons Hg_9N_4I_6+12NH_4I+(n-4)NH_3$. This compound was also made by gradually heating mercuric iodoamide between 80° and 100° when the white mass becomes brown and ammonia is evolved: $12NH_2HgI=Hg_9N_4I_6+3HgI_2+8NH_3$; the reaction is not reversible. The same compound was made by the action of a 25 per cent. soln. of sodium hydroxide, on mercuric diamminoiodide. M. François represents the formula of $3HgI_2.4NH_3$, by

$Hg_3H_4H_{12}I_6$, and he regards $Hg_9N_4I_6$ as being formed by replacing all the hydrogen by bivalent mercury, graphically :

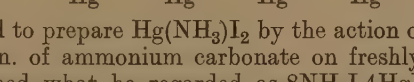


$3HgI_2.4NH_3$



$Hg_9N_4I_6$

in which two nitrogen atoms are supposed to be quinquivalent and two septivalent. M. François prepared microscopic crystals of $Hg_9H_4I_6$; and found it to be insoluble in neutral solvents, and to be transformed by conc. soda-lye into mercuric oxyiodide and dimercuriammonium iodide. M. François also prepared **heptamercuriammonium tetraiodide,** $Hg_7H_2N_4I_4$, by the action of 50 c.c. of $\frac{1}{10}N$-ammonia on $3HgI_2.4NH_3$ (eq. to 2·5 grms. of mercuric iodide) for two days with frequent stirring. The reaction is reversible. The brown crystalline mass is represented as being constituted :



L. Pesci attempted to prepare $Hg(NH_3)I_2$ by the action of ammonia on mercuric iodide ; and of a soln. of ammonium carbonate on freshly precipitated mercuric iodide, but he obtained what he regarded as $8NH_4I.4HgI_2.3NHg_2I$, *ammonium-mercuri-dimercuriammonium iodide*, but which E. C. Franklin supposes to be a slightly ammonolyzed mixture, $NH_2.Hg.I.9Hg(NH_3)nI_2$.

According to M. Adams,[3] hydroxylamine does not unite with mercuric iodide to form a complex **mercuric hydroxylamine iodide ;** the reduction of mercuric oxide to mercury by hydroxylamine hydroiodide was so rapid, even in the cold, that no intermediate products were isolated. The other methods employed in the preparation of the double salts with hydroxylamine chloride and mercuric chloride are also without avail. Hence, the reducing power of hydroxylamine or its hydrochloride increases in passing from the chloride to the iodide.

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§ 26. Double and Complex Salts of Mercuric Iodide—The Iodomercuriates

Mercuric iodide forms a series of double salts with the univalent metals $M'HgI_3$ and M'_2HgI_4—according to D. Dobrosserdoff,[1] the former are decomposed by water,

but the latter are fairly stable. The bivalent metals form salts of the types $M''Hg_2I_6$ and $M''HgI_4$. These double salts are supposed to be salts of the complex acids $HHgI_3$, H_2HgI_4, $H_2Hg_2I_6$. A. Kekulé says that hydrogen sulphide gives no precipitate when passed into a conc. soln. of mercuric iodide in hydriodic acid. According to M. Berthelot, the heat developed during the action of hydriodic acid on mercuric iodide makes it probable that **hydriodomercuric acids** are formed; thus, $HgI_2+4HI=5{\cdot}6$ Cals., and $HgI_2+8HI=5{\cdot}8$ Cals. Nearly the same amount of heat is developed as by the soln. of mercuric iodide in a soln. of potassium iodide and as is the case when hydriodic acid reacts with potassium hydroxide. P. F. G. Boullay dissolved a mol of mercuric iodide in one of warm hydriodic acid; on cooling, crystals of mercuric iodide were first deposited, and these were followed by a crop of citron-yellow transparent needles. The crystals are probably $3HgI_2.2HI.H_2O$, because M. François obtained these crystals by an analogous process. The crystals give off hydriodic acid, forming mercuric iodide when exposed to warm dry air; they are decomposed by water, forming mercuric iodide. G. Neumann evaporated a sat. soln. of mercuric iodide in hydriodic acid in a desiccator over sulphuric acid and lime at the temp. of a winter's cold. The resulting yellow needles had the composition $HgI_2.HgI$, and they became red when exposed to the air.

Four double mercuric and ammonium iodides have been prepared with the ratios $HgI_2 : NH_4I : H_2O$ as 2 : 1 : 0, 1 : 1 : 1, 1 : 2 : 0, and 1 : 2 : 1. P. F. G. Boullay [2] found that a hot aq. soln. of a mol of ammonium iodide dissolves one and a half mols of mercuric iodide; part of the latter separates out on cooling, and the remaining liquid furnishes crystals of **hydrated ammonium triiodomercuriate,** $NH_4I.HgI_2.H_2O$, or $NH_4HgI_3.H_2O$. A. Longi and G. Mazzolino also prepared the same salt from one part of a mixture of two mols of iodoform and three mols of mercuric cyanide with four of five parts of alcohol treated in a sealed tube for two days at 150°–155°, or for a shorter time at 160°–165°. Hydrogen cyanide, carbon monoxide, carbon dioxide, methane, formic acid, mercury, etc., are formed. The yellow oil also produced smells of an isonitrile, and furnishes on evaporation crystals of $NH_4I.HgI_2.H_2O$ which can be purified by recrystallization from alcohol. F. Pfankuch previously obtained these crystals, but regarded them as a double compound of cyanoform and mercuric iodide, $2CHCy_3.3HgI_2$, a conclusion which A. Claus could not verify. Hydrated ammonium tri-iodomercuriate crystallizes in yellow needles, which are stable in air, but, according to P. F. G. Boullay, in vacuo they become orange-yellow and give off 3 per cent. of water; and when heated, also, they fuse to a yellow liquid, which gives off 3 per cent. of water, and then becomes viscid and acquires a red colour—on cooling, the mass freezes to an anhydrous mass of red crystals. If heated to a still higher temp., part of the salt sublimes undecomposed, and part is resolved into mercury, mercuric iodide, etc. A. Longi and G. Mazzolino give the m.p. as 110°–111°, and say that the liquid freezes to a mass of yellow needles at 75°; they also add that the crystals lose water in open vessels at 100°, or in a stream of dry air at 65°–70°, and become orange-red. Water decomposes the crystals with the separation of 40 per cent. of mercuric iodide, and P. F. G. Boullay adds that the remaining soln. contains an excess of ammonium iodide, for it yields crystals of hydrated ammonium tri-iodomercuriate when conc. by evaporation; A. Longi and G. Mazzolino obtained crystals of approximately the composition $12NH_4I.5HgI_2$, but it is not clear if this formula is that of a compound or a mixture—probably the latter. According to M. François, in the action of water on ammonium triiodomercuriate, there is a state of equilibrium which alters with temp. less mercuric, iodide separates the higher the temp. of the water, and with a large proportion of water a soln. of mercuric iodide in ammonium iodide is formed, while with a small proportion of water, a soln. of ammonium triiodomercuriate in ammonium iodide is formed. A. Longi and G. Mazzolino say that ammonium triiodomercuriate is soluble in alcohol, and rather more soluble in ether; and that when this salt is treated with an alkali hydroxide or sulphide, ammonia is evolved.

A. Ferratini prepared **hydrated dihydrazine triiodomercuriate,** $2N_2H_4.HI.HgI_2.H_2O$, by the action of powdered mercuric iodide on a conc. soln. of the hydrazine salt. After standing two days in vacuo, the soln. deposits yellowish-white, prismatic, hygroscopic plates, which slowly decompose with the separation of mercuric iodide. The crystals melt at 92°–93°, and the dark yellow fluid solidifies and melts a second time at 152°–153°. This salt is but sparingly soluble in water, alcohol, acetone, ethyl acetate, etc.; and insoluble in ether. The aq. soln. are stable only if a very small proportion of water is present, and the salt very pure. The salt is vigorously attacked by conc. nitric acid.

S. Hajnóci and M. Löw prepared **ammonium pentaiododimercuriate,** $NH_4I.2HgI_2$, or $NH_4Hg_2I_5$, by heating a mixture of a mol of mercuric chloroamide with three of methyl iodide in a sealed tube for 10 to 12 hrs. at 100°. This salt forms an aggregate of light yellow crystals which can be separated from the mercuric methyl monamminoiodide, $HgI_2(CH_3)NH_2$, and other products by fractional crystallization from nitrobenzene. When gently warmed in a sealed tube mercuric iodide sublimes, and with stronger heating ammonia gas is evolved. Water decomposes the salt with the separation of mercuric iodide; and it is soluble in an aq. soln. of potassium iodide; and very soluble in alcohol, ether, and nitrobenzene.

A. G. Duboin made a heavy liquid of sp. gr. 2·98 (26°) and refractive index 1·527—sodium light—by alternately adding mercuric and ammonium iodides to a small quantity of water until sat. The soln. deposits crystals of **hydrated ammonium tetraiodomercuriate,** $2NH_4I.HgI_2.H_2O$, or $(NH_4)_2HgI_4.H_2O$. H. St. C. Deville and L. Troost found the vapour density of $2NH_4I.HgI_2$ to be 6·49 at 360°, and 6·38 at 440°. A. G. Duboin [3] prepared a heavy liquid of sp. gr. 3·28 at 25·63°, and refractive index 1·783—sodium light—by alternately adding mercuric and lithium iodides to a small quantity of water until sat. The soln. gives a precipitate of mercuric iodide with water, but is soluble in alcohol. On standing, the soln. deposits **hexahydrated lithium tetraiodomercuriate,** $2LiI.HgI_2.6H_2O$, or $Li_2HgI_4.6H_2O$, in the form of long, flattened, deliquescent needles, having a sp. gr. 3·26 at 0°, readily soluble in methyl, ethyl, propyl, isopropyl, isobutyl, amyl, or allyl alcohol, glycerol, acetaldehyde, acetone, formic or acetic acid, ethyl acetate, or oxalate, or ether; less soluble in nitrobenzene, ethylene bromide, or chloroform; insoluble in benzene or methyl iodide; and decomposed by water. The mother liquor from which the crystals have been removed yields at 8° a second **octohydrated lithium tetraiodomercuriate,** $Li_2HgI_4.8H_2O$, or $2LiI.HgI_2.8H_2O$, in the form of large, soft, prismatic crystals, melting in the hand, having a sp. gr. 2·95 at 0°, closely resembling the first compound in solubility, but insoluble in ethylene bromide and almost so in nitrobenzene. F. Calzolari and U. Tagliavini prepared the hexamethylenetetramine derivative of A. G. Duboin's salt. J. E. Marsh prepared a number of compounds of mixed lithium halogenomercuriates with ethyl ether—*e.g.* $LiBr.HgBr_2.4(C_2H_5)_2O$; $LiBr.HgCl_2.(C_2H_5)_2O$; $LiCl.HgBr_2.(C_2H_5)_2O$; $LiI.HgI_2.6(C_2H_5)_2O$; $LiI.HgBr_2.5(C_2H_5)_2O$; $LiBr.HgI_2.4(C_2H_5)_2O$.

According to P. A. von Bonsdorff,[4] the evaporation of an aq. soln. of sodium iodide sat. with mercuric iodide over sulphuric acid in a desiccator furnishes deliquescent yellow rhombic prisms of a double iodide of sodium and mercury whose composition was not determined but was possibly, $2NaI.HgI_2$. About the same time, P. F. G. Boullay noted that a hot soln. of two mols of sodium iodide in a little water dissolves over three mols of mercuric iodide, and on cooling some of the latter separates out. The evaporation of the mother-liquid gives a yellow mass which is not crystalline, and which probably contains some yellow mercuric iodide, because when the inner surface of the basin is scratched with a glass rod, red mercuric iodide appears to be formed; if this be dissolved in warm water, more mercuric iodide separates out on cooling, and the mother liquid, when evaporated slowly, gives deliquescent needle-like crystals—probably **sodium tetraiodomercuriate,** $2NaI.HgI_2$, but no analyses were given. J. B. Berthemot attempted to make the double salt by boiling mercuric iodide with aq. or alcoholic sodium

hydroxide, or sodium carbonate ; or by boiling mercuric or mercurous oxide with aq. sodium iodide he obtained a deliquescent mass, but not definite crystals.

A. G. Duboin prepared a heavy liquid of sp. gr. 3·46 at 26°, and refractive index 1·797—sodium light—by alternately adding mercuric and sodium iodides to a small quantity of water until sat. The soln. absorbs a little moisture from the air, and gives a precipitate of mercuric iodide when mixed with a large proportion of water ; the liquid is soluble in alcohol, aldehyde, acetone, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, ethyl benzoate ; and insoluble in benzene, monochlorobenzene, chloroform, ethylene bromide, and ethyl nitrate. Cellulose swells up and becomes transparent when placed in this liquid, and when the product is washed with an aq. soln. of sodium iodide, it dries to a horny mass. When A. G. Duboin's soln. is very slowly—"some weeks"—evaporated in dry air, it furnishes deliquescent flattened crystals of **tetrahydrated sodium tetraiodomercuriate,** $2NaI.HgI_2.4H_2O$, which have a sp. gr. of about 3 at 0°. E. Rupp prepared the anhydrous salt, $2NaI.HgI_2$, by the action of an alkaline soln. of iodine on mercuric cyanide.

P. F. G. Boullay found that a boiling soln. of two mols of potassium iodide dissolved three mols of mercuric iodide, and deposited on cooling one mol of mercuric iodide, but not so much in the presence of alcohol. A. Souville and F. Labouré [5] got over two, but not so much as three mols of mercuric iodide in a soln. with two mols of potassium iodide, and it was therefore argued that the compound $2KI.3HgI_2$ is not formed in the soln., but that mercuric iodide is dissolved in a soln. of $KI.HgI_2$, since on evaporation it yields needle-like crystals of this salt and cubes of potassium iodide. C. J. Tanret found that a soln. of 10 grms. of potassium iodide in 100 grms. of water dissolved 14·73 grms. of mercuric iodide at 20°. M. François noted a break in the solubility curve of mercuric iodide in soln. of potassium iodide, as illustrated in Fig. 31, which represents as abscissæ the number of grams of potassium iodide per 100 c.c. of liquid ; likewise with mercuric iodide as ordinates. A selection of his numbers, at 20°, is :

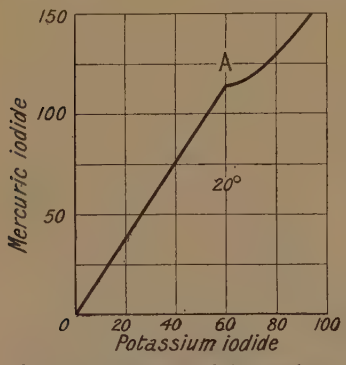

Fig. 31.—Effect of Potassium Iodide on the Solubility of Mercuric Iodide.

KI . .	8·665	30·440	52·436	62·814	63·036	71·427	82·746	94·104
HgI_2 . .	13·72	55·09	94·09	116·45	116·22	120·76	131·88	145·7

The break, *A*, in the curve for 62·8 grms. of potassium iodide and 116·2 grms. of mercuric iodide is attributed to the change in the solid phase from HgI_2 to $KI.HgI_2$.

The solubility of mercuric iodide in aq. soln. of potassium iodide has been long explained by assuming that a soluble double or complex salt is formed. M. S. Sherrill examined the nature of the complex salts (i) from measurements of the e.m.f. of conc. cells of the type $Hg \mid HgI_{2\text{soln. }a}, HgI_{2\text{soln. }b} \mid Hg$; (ii) from the effect of mercuric iodide on the f.p. of soln. of potassium iodide ; (iii) from the distribution of mercuric iodide between benzene and aq. soln. of potassium iodide ; G. Bredig and J. H. Walton (iv) from the effect of mercuric iodide on the catalytic decomposition of hydrogen peroxide by soln. of potassium iodide on the assumption that the velocity of the decomposition is proportional to the conc. of iodine-ions which is diminished in the presence of mercuric iodide ; H. M. Dawson (v) from the partition of mercuric iodide between water and carbon disulphide or carbon tetrachloride ; E. Rieger (vi) from the conductivity of soln. of potassium mercuric iodide being smaller than the sum of the conductivities of the constituents ; and R. Abegg, C. Immerwahr, and F. Jander (vii) from the solubility of mercuric iodide in soln. of potassium iodide, where the mol. ratio $KI : HgI_2$ for soln. sat. with

mercuric iodide falls from 2·2 for a 0·031*N*-soln. to 1·82 for a *N*-soln. of potassium iodide. The general conclusion is that the soln. contain the complexes $2KI.HgI_2$ and $3KI.2HgI_2$. Expressing the components in the order $HgI_2 : KI : H_2O$, the five salts 1 : 1 : 0, 1 : 1 : 1, 1 : 1 : 1½, 2 : 1 : 0, and 2 : 1 : 2 have been reported.

A. C. Dunningham has studied the three-component system HgI_2—KI—H_2O at 20° and at 30°, and his results are plotted in Fig. 32. There is no evidence of the formation of mixed crystals with potassium and mercuric iodides; and the following four solid phases, KI, $KHgI_3$, $KHgI_3.H_2O$, and HgI_2, were alone found to exist in equilibrium with the soln. The point *E* represents water; *F*, potassium iodide; *G*, mercuric iodide; *M*, potassium triiodomercuriate, $KHgI_3$; and *N*, monohydrated potassium triiodomercuriate, $KHgI_3.H_2O$. The line *AB* represents the range of sat. soln. coexisting with solid potassium iodide; *BC*, with solid potassium triiodomercuriate; *CD*, with solid hydrated potassium triiodomercuriate; and *DE*, with solid mercuric chloride. The point *B* represents a sat. soln. coexisting with solid potassium iodide and triiodomercuriate; *C*, with solid potassium triiodomercuriate and its monohydrated salt; and *D*, with solid hydrated potassium triiodomercuriate and mercuric iodide. The area *FAB* represents mixtures of the sat. soln. on *AB* and solid potassium iodide; *BCM*, on *BC* and solid iodomercuriate; *CND*, and *CD* and solid hydrated potassium triiodomercuriate; *EDG*, on *DE* and solid mercuric iodide; *FBM*, mixtures of soln. *B* and solid potassium iodide and triiodomercuriate; *MCN*, soln. *C* and solid potassium iodomercuriate and its monohydrated salt; *NDG*, of soln. *D* and solid hydrated potassium triiodomercuriate and mercuric iodide; and *MNG*, solid mixtures of mercuric iodide, potassium triiodomercuriate and its monohydrate. When solid mercuric iodide is added to a sat. soln. of potassium iodide, represented by *A*, the composition of the mixture follows the line *AG*. The first solid phase which separates is hydrated potassium triiodomercuriate, $KHgI_3.H_2O$. A. C. Dunningham also studied the ternary systems: potassium iodide, ether, and water at 20°; mercuric iodide, ether, and water; and potassium and mercuric iodides and ether at 20°, and again found the range of the existence of potassium iodomercuriate, $KHgI_3$, but of no other iodide. He also worked out the conditions of equilibrium of the four-component or quaternary system: mercuric and potassium iodides, ether, and water.

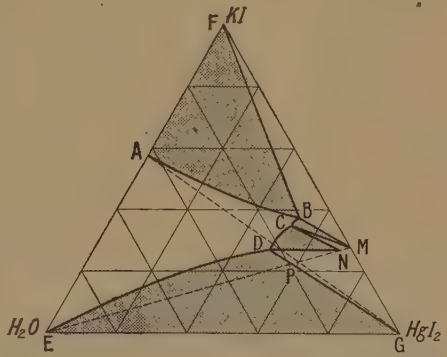

FIG. 32.—A. C. Dunningham's Equilibrium Diagram for the Ternary System, HgI_2—KI—H_2O.

P. F. G. Boullay obtained crystals of **potassium triiodomercuriate,** $HgI_2.KI$, or $KHgI_3$, by cooling a hot sat. soln. of mercuric iodide in potassium iodide until one-third the mercuric iodide which was in soln. had separated out; by further cooling the mother liquor, prismatic crystals of this salt were said to be formed. If mol. proportions of the component salts be used, W. A. H. Naylor and E. J. Chappel say that a mixture and not a compound is formed. P. A. von Bonsdorff evaporated a soln. of potassium iodide, sat. in the cold with mercuric iodide, in dry air, or over sulphuric acid in a desiccator, and obtained crystals of this salt; he also evaporated a soln. of mercuric chloride in potassium iodide until crystallization occurred, and extracted the double salt with alcohol—potassium chloride remained as an insoluble residue. J. B. Berthemot likewise prepared yellow crystals of this salt on cooling the liquid obtained by boiling mercuric iodide with alcoholic potassium hydroxide or carbonate; and also by boiling mercuric oxide with an aq. soln. of potassium iodide, so that the proportion of mercuric to potassium iodide is as 1 : 1, the liquid

contains potassium hydroxide and deposits crystals of $KI.HgI_2$. If mercurous oxide is used some mercury is formed, and if the oxide be in excess, some mercurous iodide as well. According to J. E. Marsh and R. de J. F. Struthers, this salt can be extracted from an aq. soln. of $2KI.HgI_2$ by ether, ethyl formate, or other solvents.

Potassium triiodomercuriate forms long yellow prismatic crystals similar to the ammonium salt. M. Berthelot gives the heat of formation from red mercuric iodide as 2·1 Cals., and from the yellow, 5·1 Cals. P. F. G. Boullay says that when the salt is heated it loses a little water, and melts to a red liquid from which mercuric iodide sublimes. R. Brandes and G. Böhm said that if the temp. is not too high the molten liquid is yellow and solidifies to a greenish-yellow mass with a radiating fracture; at a higher temp. the liquid is brown, and the solid has a granular fracture; at a still higher temp. the molten salt is dark brown, and gives off mercuric iodide. The mol. lowering of the f.p. of aq. soln. was found by F. M. Raoult to be 90°. According to P. F. G. Boullay, water separates about half the mercuric iodide, and forms a soln. of $2KI.HgI_2$. This is probably a wrong inference. According to A. C. Dunningham's work, if water be added to potassium iodomercuriate, $KHgI_3$, the composition of the mixture can be represented by points on the line *ME*, Fig. 32. When *N* is reached, all the salt is converted into hydrated potassium iodomercuriate; further additions of water cause the formation of soln. *D* with the two solid phases, mercuric iodide and hydrated potassium iodomercuriate; at *P*, all the last-named salt is decomposed and mercuric iodide alone appears as solid phase. The mixture then follows the line *DE*, more and more mercuric iodide being formed as the proportion of water increases, until, at *E*, the soln. is virtually pure water, for the solubility of mercuric iodide can, for the present purpose, be regarded as negligibly small. P. F. G. Boullay states that dil. acids separate all the mercuric iodide from potassium iodomercuriate. J. B. Berthemot and P. F. G. Boullay say that although conc. acetic acid dissolves neither of the component salts, it does dissolve the double salt, and the double salt also dissolves in ether; the addition of water to the alcoholic soln. precipitates mercuric iodide, but R. Brandes and G. Böhm said that the alcoholic soln. may be mixed with the ethereal soln. without precipitation; and that a soln. in 70 per cent. alcohol deposits crystals of mercuric iodide during spontaneous evaporation. A. C. Dunningham, and J. E. Marsh have made a special study of the action of ether on this salt—a double salt, $KHgI_3.4(C_2H_5)_2O$, is formed. R. Brandes and G. Böhm also found the salt to be permanent in dry air, but hygroscopic in moist air; and if a thin film of the salt be formed on a watch-glass by the evaporation of its alcoholic soln., the colour is red when breathed upon, and the yellow colour is restored when gently heated. W. Pawloff found that the crystals sinter at 69°; they become red at 72°–80°; and they begin to volatilize at 104·5°. The molten salt if shaken freezes at 105°, but otherwise it remains liquid down to 85°, when it solidifies and the temp. rises to 104·5°. The last traces of water are expelled at 191°–193°, and it decomposes at 204° into its components; P. Walden and M. Centnerszwer say the salt melts at 117° to a red liquid, and that it loses over one per cent. in weight when heated to 98°, but the loss of weight is not constant because some mercuric iodide is lost by volatilization along with the water. M. Berthelot gives the heat of formation from red mercuric iodide as 2·3 Cals. and from the yellow iodide 5·3 Cals. According to P. F. G. Boullay, mercury distils from a heated mixture of potassium triiodomercuriate and copper or iron; chlorine decomposes the heated salt, and potassium chloride remains.

W. Pawloff prepared **hydrated mercuric triiodomercuriate,** $KHgI_3.N_2O$, by crystallization from a soln. of equimolar parts of the component salts evaporated in a desiccator; and when a mixture of the component salts is allowed to stand for a few weeks in contact with undried ether this double salt is formed. P. Walden and M. Centnerszwer crystallized the commercial salt from a boiling mixture of acetone and benzene, and evaporated the soln. slowly at ordinary temp. The lower deep-red layer of liquid furnishes crystals of this salt which can be dried at

ordinary temp. The crystals are straw-yellow hygroscopic prisms or needles. The limits of stability of the salt in contact with water are indicated in Fig. 32. All are agreed that the salt is decomposed by water; and J. E. Marsh says that when the yellow crystals are moistened with water they become red—presumably owing to the formation of red mercuric iodide, but he says that the crystals can be dissolved in a little water, and that the liquid obtained by heating the salt to 117° is a soln. of the salt in its water of crystallization. W. Pawloff found that the salt is not decomposed by dissolving it in alcohol or acetone. J. E. Marsh says that the salt is not very soluble in dried ether, but is easily soluble in undried ether; that the solubility is greater in cold than in warm ether; and that the soln. in ether is accompanied by the development of heat, and the formation of a compound, $KHgI_3.4(C_2H_5)_2O$.

W. A. H. Naylor and E. J. Chappel claim to have made the sesquihydrated salt, $KHgI_3.1\frac{1}{2}H_2O$, by dissolving 45 grms. of mercuric iodide and 16·5 grms. of potassium iodide in 20 c.c. of boiling 90 per cent. alcohol. Yellow crystals of the salt separate out during the cooling of the filtered soln. E. G. Clayton also obtained similar crystals by allowing a conc. soln. of Nessler's reagent to stand for some time. The crystals were washed with alcohol and dried. M. François also obtained this same salt. There is, however, some doubt if this hydrate really exists.

P. F. G. Boullay assumed *potassium tetraiodomercuriate*, $2KI.HgI_2$, or K_2HgI_4, to be present in the liquid obtained by dissolving potassium triiodomercuriate in water, when he supposed that half the mercuric iodide separates out. On evaporation, the soln. furnished a yellow mass but no crystals; when treated with water, the yellow mercuric iodide remains undissolved, but is dissolved on shaking the mixture. Both A. Souville and F. Labouré showed that the soln. contains not the tetraiodomercuriate, but is rather a soln. of potassium iodide in one of potassium triiodomercuriate. W. Pawloff says that if the component salts are present in aq. soln. in the ratio $HgI_2 : 2KI$, crystals of the double salt, $HgI_2.2KI.2H_2O$, are formed. S. M. Jörgensen has said that if a soln. of iodine in one of potassium iodide be shaken with mercury, part of the iodine forms insoluble mercurous iodide and the remainder goes into soln. as $2KI.HgI_2$. J. M. Thomson and W. P. Bloxam say that this salt separates from a supersaturated soln. when seeded with needle-like crystals of mercuric iodide, but not with crystals of potassium iodide. E. Rupp made it by the action of hydrochloric acid and potassium iodide on mercuric cyanide or chloride; E. Rupp and W. F. Schirmer, by the action of potassium iodide on mercuric oxide, and they propose a method for determining mercuric oxide in ointments by dissolving the oxide in water containing 8–12 times its weight of potassium iodide, and titrating the soln. with $\frac{1}{10}N$-HCl, using methyl orange as indicator. L. L. de Koninck and J. Lebrun also base a method for the volumetric determination of mercuric chloride by titration with potassium iodide; the separation of mercuric iodide, say F. Auerbach and W. Plüddemann, begins when this double salt, $2KI.HgI_2$, is formed: $HgCl_2+4KI=HgI_2.2KI+2KCl$; but there is a slight error owing to the separation of mercuric iodide before all the mercury salt required for the last-named reaction has been added; this is due to the secondary reaction, $HgI_2.2KI+HgCl_2 \rightarrow 2HgI_2+2KCl$, which depends on the relative concentrations of the salts in soln., and for which a correction can be made. J. E. Marsh and R. de J. F. Struthers made this salt by the action of different ketones—acetone, diethylketone, acetophenone, etc.—on a soln. of mercuric iodide in cold potash-lye. R. G. van Name and W. G. Brown studied the equilibrium of soln. of potassium and mercuric iodides, and obtained evidence of the formation of the double salt $2KI.HgI_2$.

The facts are not very definite as to the formation of $2KI.HgI_2$, since most of them can be interpreted by assuming that soln. of mercuric iodide in potassium iodide are formed, and there is the very clear evidence of A. C. Dunningham that this salt does not exist in aq. soln. between 20° and 30°. Consequently, the reaction etc., said to be due to the formation and properties of this salt really refers to a

soln. or mixture of potassium iodide with potassium triiodomercuriate. For example, J. Thomsen gave the heat of soln. of a mol of mercuric iodide in two of potassium iodide as 3·45 Cals., and the heat of soln. of the salt in 800 mols of water, as —9·81 Cals. E. Rieger found the electrical conductivity of 0·214 mol of mercuric iodide and 0·782 mol of potassium iodide per litre to be $7{\cdot}0\times10^{-4}$. R. Behrend studied the e.m.f. of aq. soln. of the salt. F. Bezold said that the salt is copiously soluble in methyl acetate, and that hydrogen sulphide does not change the soln.; dry ammonia produces no change; but hydrogen sulphide in the soln. sat. with ammonia produces a red precipitate of mercuric sulphide. E. Alexander and M. Hamers found a similar behaviour with soln. in ethyl acetate. By electrolyzing a soln. of the salt in liquid sulphur dioxide, L. S. Bagster and B. D. Steele obtained a precipitate containing sulphur on the cathode. J. M. Eder and G. Ulm warmed the aq. soln. for a long time with sodium thiosulphate at 80°, and obtained a voluminous precipitate—a mixture of mercurous iodide and mercuric sulphide. H. Wegelius and S. Kilpi removed iodine from the soln. by the addition of moist silver chloride, and they noted the formation of **silver tetraiodomercuriate,** Ag_2HgI_4, which below 50° is yellow, and red above this temp. H. Ley and G. Wiegner prepared a white potassium diamminotetraiodomercuriate, $K_2HgI_4.2NH_3$, by the action of ammonia gas on potassium tetraiodomercuriate. The compound loses its ammonia after seven hours' exposure in vacuo, and becomes red. W. Peters found the vapour tension rises from 17 mm. at 0° to 272 mm. at 55°. Numerous compounds of mercuric iodide with organic compounds have been reported —*e.g.* A. Naumann's compound with benzonitrile, $KHgI_5.5C_6H_5.CN$; etc.

F. Hofmeister has studied the action of this salt on albumen. C. J. Tanret recommended the salt K_2HgI_4 as a reagent for albumenoids; and F. L. Winckler, W. Delffs, J. E. de Vrij, W. R. Grove, F. F. Mayer, C. J. Tanret, F. A. Flückiger, G. Herkel, I. Guareschi, etc., have recommended the same reagent on account of the colour reactions it produces with alkaloids. G. Romijn [6] has recommended the alkaline soln. as an oxidizing agent. An aq. soln. of potassium and mercuric iodides can be made with a sp. gr. 3·196, and glass floats on the liquid. The soln. has been recommended by A. H. Church, J. Thoulet, V. Goldschmidt, J. Joly, and others for separating a mixture of minerals above and below the sp. gr. of the liquid. According to V. Goldschmidt, the soln. is best prepared in the following manner:

Stir 305 grms. of mercuric iodide and 246 grms. of potassium iodide with as little water as is necessary for the soln. of the salts. The ratio $KI : HgI_2$ is as 1 : 1·239, and this proportion gives the best result. The liquid is evaporated on the water-bath until a piece of tourmaline, sp. gr. 3·1, floats on it, the liquid is allowed to cool, and its sp. gr. will be nearly 3·196 in winter, 3·17 in summer. Acicular crystals of a hydrated double salt separate on cooling; the precipitate can be dissolved in a few drops of water, or it can be filtered off, dissolved in water, and evaporated to the necessary concentration. If too much potassium iodide be used, crystals separate on the surface of the liquid; and if too much mercuric iodide be used, a mass of yellow needles separates; this can be dissolved in water, but red mercuric iodide is simultaneously deposited, and is dissolved by agitation with a soln. of potassium iodide.

The conc. soln. is decomposed by adding water, and red mercuric iodide is deposited, but redissolved on agitating the mixture. The sp. gr. changes on long standing owing to the absorption of moisture from the air. The sp. gr., D, of the soln. with W grms. of the solid salt to 100 grms. of water is:

D	2·940	2·717	2·243	1·873	1·546	1·247	1·193	1·139	1·091	1·0477
W	617·24	466·96	255·2	150·6	83·0	33·9	25·809	18·205	11·677	6·001

The soln. is not affected by exposure to light. H. S. Hatfield, however, found that if iron compounds be present, the reaction: $2KI+O+Hg+H_2O=2KOH+HgI_2$, occurs in sunlight, since under these conditions iron compounds are strong catalytic agents. The soln. is decomposed by organic matter—filter paper, etc. The

liquid is poisonous, and attacks the skin. Metals—derived from the grinding apparatus, etc.—decompose the soln. with the separation of mercury. It is difficult to wash the heavy soln. from the particles of minerals, and some minerals—*e.g.* felspar, chrysocoll, zeolites, clays, and colloids—decompose or adsorb the soln. very tenaciously. The conc. soln. are very viscid, and the viscosities have been measured by E. Clerici; and A. G. Duboin has measured the refractive indices—a soln. of sp. gr. 3·196 (22·9°) has a refractive index 1·730—for the Na-line.

An alkaline soln. of the double potassium and mercuric iodide—called **Nessler's solution**—is used for the colorimetric determination of ammonia, for it gives a yellow or brown coloration with ammonia or ammonium salts, and the intensity of the colour is proportional to the concentration of the ammonia present. The precipitate with Nessler's reagent is supposed to be mercuric hydroxyiodoamide: $NH_3+2K_2HgI_4+3KOH=7KI+2H_2O+HgOH.NH.HgI$. Several methods of preparing the reagent have been published in analytical works. A litre of Nessler's soln. is usually made by dissolving 60 grms. of potassium iodide in 100 c.c. of water and pouring this soln. on 25 grms. of mercuric chloride in a glazed porcelain mortar. The mixture is triturated until all is dissolved, and the soln. made up to 750 c.c. by the addition of water. Add 150 grms. of potassium hydroxide in sticks, and, when dissolved and cooled, gradually add sufficient of a sat. soln. of mercuric chloride to produce a slight permanent precipitate; dil. the soln. to a litre; and, after it has stood for some time to let the precipitate settle, decant off the clear liquid. The soln. is preserved in a bottle closed with a well-fitting rubber stopper. C. J. Tanret [7] mixed 14·73 grms. of mercuric iodide with a soln. of 10 grms. of potassium iodide in 100 grms. of water, and added half its volume of a 1 : 3 soln. of sodium hydroxide. G. Egeling says that the presence of mercuric chloride raises the sensitiveness of the reagent, but sodium or potassium chloride has no result. L. L. de Koninck says that Nessler's reagent does not give a coloration or a precipitate with ammonia in absolute alcohol soln.; and the presence of alcohol in the aq. soln. hinders the reaction; the corresponding reaction with mercuric chloride resulting in the formation of mercuric chloroamide, $Hg(NH_2)Cl$, is not so much affected by the presence of alcohol. C. J. Tanret says that the ammonia reaction is not presented with methyl- or ethyl-amine, but K. W. Charitschkoff says that the amine hydrochlorides which are decomposed by aq. soln. of potassium iodide do give the reaction. L. Rosenthaler noted that organic compounds with primary or secondary hydroxyl groups are reduced, while those with tertiary hydroxyl groups are not reduced by J. Nessler's reagent. Various other organic compounds were found by J. Vamvakas, H. Ditz, E. Schulze, P. N. Raikow and C. Külümoff, etc., to reduce Nessler's reagent—gelatine, for instance, gives a lead-coloured emulsion; gum arabic also gives a grey precipitation which is prevented by tartaric acid.

H. Erdmann,[8] and H. Grossmann obtained yellow prisms or needles by cooling a soln. of mercuric iodide in hot conc. rubidium iodide. H. Grossmann found them to be **rubidium triiodomercuriate,** $RbHgI_3$, or $RbI.HgI_2$. They are immediately decomposed by water with the separation of mercuric iodide; they dissolve without decomposition in alcohol; they are readily soluble in acetic acid, and behave chemically like the other alkali complexes with mercuric iodide. H. Grossmann made yellow lustrous four-sided plates of **rubidium tetraiodomercuriate,** $2RbI.HgI_2$, or Rb_2HgI_4, from a soln. with the component salts in mol. proportions. The crystals become matt on exposure to air, and are easily soluble in water. H. Grossmann also obtained yellow plates of **rubidium dibromodiiodomercuriate,** $Rb_2HgBr_2I_2$, or $2RbBr.HgI_2$, from a soln. of mercuric iodide in rubidium bromide; the crystals are decomposed by water into their component salts; but they dissolve in alcohol without decomposition.

H. L. Wells [9] prepared five cæsium iodomercuriates, Cs_3HgI_5; Cs_2HgI_4; $CsHgI_3$; $Cs_3Hg_3I_8$; and $CsHg_2I_5$. The corresponding chlorides and bromides of all except $Cs_2Hg_3I_8$ have been made, but no iodide or bromide corresponding with $CsHg_5Cl_{11}$. It is suggested by H. L. Wells that J. Holmes' ammonium octochlorotrimercuriate, $(NH_4)_2Hg_3Cl_8.4H_2O$, is the same type of compound as the salt $Cs_2Hg_3I_8$. According to H. L. Wells, the double iodides of mercury and cæsium are all yellow. The colour of the salts $CsHg_2I_5$ and $Cs_2Hg_3I_8$, resembles normal potassium chromate, and the others become paler as the proportion of the cæsium salt increases. All of them are decomposed by water, forming compounds containing more mercuric iodide than the original salt, or, at the limit,

mercuric iodide itself. It is therefore possible to take any one of these double salts, and, by recrystallizing from water and evaporating the resulting soln. to prepare the complete series of five double iodides, as well as the component simple iodides, without the use of any new material. It is noticeable that the iodides differ from the chlorides and bromides in not including a salt that can be recrystallized continually from water. This peculiarity is doubtless due to the comparative insolubility of mercuric iodide.

The salt **cæsium pentaiodomercuriate,** Cs_3HgI_5, or $3CsI.HgI_2$, is prepared like the corresponding chloride and bromide by crystallization—by cooling or spontaneous evaporation—from very conc. soln. of cæsium iodide with but a small proportion of mercuric iodide. S. L. Penfield says the crystals are of diverse habit and belong to the rhombic bisphenoidal system with axial ratios $a:b:c = 0{\cdot}5362:1:0{\cdot}97975$; H. L. Wells gives the sp. gr. 4·605. When this salt is dissolved in a small quantity of hot water, **cæsium tetraiodomercuriate,** Cs_2HgI_4, or $2CsI.HgI_2$, crystallizes out on cooling, but with a larger proportion of water, everything remains in soln.; the same salt is produced under wide limits of conditions by cooling mixed soln. of the component salts with the cæsium iodide in excess. The crystals have diverse habits, and belong to the monoclinic system; S. L. Penfield gives the axial ratios $a:b:c=1{\cdot}3155:1:0{\cdot}9260$, and $\beta=69°\ 56'$. According to T. V. Barker, these crystals are isomorphous with ammonium selenate, $(NH_4)_2SeO_4$. The sp. gr. is 4·806. The salt is not dissolved or decomposed by alcohol; but it is decomposed by water giving either one of the salts containing mercuric iodide or mercuric iodide alone; all depends on the proportion of water used. The salt **cæsium triiodomercuriate,** $HgI_2.CsI$, or $CsHgI_3$, is formed only within narrow limits of concentration from soln. with a little more mercuric iodide or water than the two preceding salts. It is easiest to dissolve Cs_2HgI_4 in a little hot water, and on cooling the salt $CsHgI_3$ can be obtained, although it often happens that all three salts: $Cs_2Hg_3I_8$, $CsHgI_3$, and Cs_2HgI_4, are successively deposited from the soln.; and it is difficult to isolate $CsHgI_3$ in a pure state. The crystals form thin transparent plates; the crystal angles have not been measured. When the crystals are pressed on paper they rapidly become opaque, but H. L. Wells says "he was unable to determine whether this is caused by mol. rearrangement or loss of water of crystallization." An air-dried sample after press. on paper had no water of crystallization, whereas a sample quickly dried on paper had a composition in agreement with $CsHgI_3.H_2O$. The salt **cæsium octoiodotrimercuriate,** $2CsI.3HgI_2$, or $Cs_2Hg_3I_8$, is formed under widely varying conditions; and is most conveniently made by cooling a soln. of Cs_2HgI_4 in the proper quantity of hot water, or by treating the same salt with not too much cold water. The monoclinic crystals vary considerably in habit, triangular plates and elongated prisms are common forms. S. L. Penfield gives the axial ratios $a:b:c=0{\cdot}3438:1:0{\cdot}3544$, and $\beta=71°\ 55{\cdot}5'$. The sp. gr. is 5·14. The salt dissolves in alcohol and is decomposed by water with the separation of mercuric iodide. If a hot aq. soln. of cæsium iodide is sat. with mercuric iodide, **cæsium pentaiododimercuriate,** $CsHg_2I_5$, or $CsI.2HgI_2$, contaminated with more or less mercuric iodide or $Cs_2Hg_3I_8$ is separated out on cooling, but if dil. alcohol be used as solvent, this salt is readily formed in yellow prisms, which become red on standing in the aq. mother liquid; they are more stable in alcoholic soln., but when dried by pressing on paper they quickly become red without losing their crystal form. The decomposition products are probably HgI_2 and $Cs_3Hg_2I_8$. The crystal angles have not been measured.

H. L. Wells has made three double salts with bromine and iodine, *viz.* $Cs_3HgBr_3I_2$; $CsHgBr_2I_2$; and $CsHgBrI_2$; and one chloroiodide, $Cs_2HgCl_2I_2$. When attempts were made to prepare bromoiodides with a larger proportion of iodide, there was an interchange of the halogen, and nearly pure double iodides were formed. **Cæsium tribromodiiodomercuriate,** $Cs_3HgBr_3I_2$, or $3CsBr.HgI_2$, forms rhombic bisphenoidal crystals like those of Cs_3HgI_5, with a pale yellow colour; **cæsium dibromodiiodomercuriate,** $Cs_2HgBr_2I_2$, or $2CsBr.HgI_2$, forms

monoclinic crystals like those of Cs_2HgI_4, with a faint tinge of yellow. This salt is possibly dimorphic, although only one form has yet been prepared. When the hot soln. cools, thin plates resembling those of the chloride, bromide, or chlorobromide are deposited first, and when the dilution is right, these crystals can be removed and stout monoclinic crystals like the iodide obtained. Only one form of **cæsium bromodiiodomercuriate,** $HgI_2.CsBr$, or $CsHg.BrI_2$, has been prepared in pale yellow monoclinic crystals with axial ratios $a:b:c=0{\cdot}978:1:0{\cdot}743$, and $\beta=87°\,3{\cdot}5'$. Only one form is known, although the three other salts of the 1 : 1 type are dimorphous. **Cæsium dichlorodiiodomercuriate,** $2CsCl.HgI_2$, or $Cs_2HgI_2Cl_2$, is the only known chloroiodide ; when attempts were made to prepare chloroiodides with more mercuric iodide, there was an interchange of halogens and a nearly pure iodide was formed. The salt $Cs_2HgCl_2I_2$ is formed only in very conc. soln. containing a great excess of the cæsium halide. It occurs in white slender radiating needles which instantly become red in contact with water owing to the formation of mercuric iodide. The crystals belong to the monoclinic system. The angles were not measured.

Three cuprous iodomercuriates have been reported with $HgCl_2:CuI$ in the mol. proportions 1 : 1, 1 : 2, and 1 : 4. P. Hess [10] obtained what he regarded as **cuprous triiodomercuriate,** $CuI.HgI_2$, or $CuHgI_3$, by treating a soln. of the corresponding potassium salt, $KHgI_3$, with cupric sulphate, decanting off the clear liquid, and washing the precipitate first with a dil. soln. of sodium thiosulphate, and later with distilled water, until iodine no longer appears in the washings. The precipitate was then dried over sulphuric acid in a desiccator. The madder-red product can be recrystallized from hydrochloric acid. E. Meusel, and E. Lenoble worked in a similar manner, but washed out the iodine with water only. S. M. Jörgensen also prepared a cuprous mercuric iodide, of unknown composition, by shaking mercury with a soln. of cupric polyiodide. L. Cramer made cuprous triiodomercuriate by the action of a dil. soln. of mercuric chloride, on an emulsion of cuprous iodide. The red powder is chocolate brown when heated to 70°, and the original colour is restored on cooling. The electrical conductivity of the solid was found by S. P. Thompson to be a maximum between 87·5° and 88·5° at which temp. the compound changes in colour from red to black. P. Hess found no chemical change occurs when heated to 100°, but at 150° mercuric iodide is evolved, and is completely expelled at a higher temp. ; iodine is simultaneously given off, but the iodine is completely expelled only by repeatedly heating the powder with nitric acid.

M. Bellati and R. Romanese prepared **cuprous tetraiodomercuriate,** $2CuI.HgI_2$, or Cu_2HgI_4, from a mixture of cuprous and mercuric iodides in alcoholic soln. ; and E. Caventou and J. E. Willm, by the action of cupric sulphate on a boiling soln. of potassium iodomercuriate. The sp. gr. of the product is 6·0956 at 0° ; the calculated value from the mixture law is 5·268, and there is accordingly a considerable contraction during the formation of the compound. M. Bellati, S. Lussana, and R. Romanese found that the colour changes from a bright red to a dark purple at 69·6° ; to a chocolate brown at 70·6° ; on cooling, the reverse changes occur at respectively 61·5°, 57·2°, and between 55·2° and 52·3°. The thermal expansion when θ is below 62° is $v=1+0{\cdot}0000784\,60\theta$; and when θ is above 72°, $v=1{\cdot}006803+0{\cdot}000\,081\,472\,8\theta$. There is an irregularity in the volume changes between 62° and 72°. The mean sp. ht. between θ_1 and θ_2 is $0{\cdot}0532068+0{\cdot}000\,041\,131(\theta_1+\theta_2)$; and the true sp. ht. at θ is $0{\cdot}0532068+0{\cdot}000\,082\,262\theta$. The heat of transformation at 70° is 2·3619, and at 60°, 2·3210 cals. E. Caventou and J. E. Willm found that a cold soln. of potassium iodide slowly extracts mercuric iodide and leaves cuprous iodide while a hot soln. acts more quickly. W. Peters prepared the red diammino-compound by the action of ammonia gas on the dried salt ; H. Ley and G. Wiegner, and W. Peters prepared green **cuprous hemiheptammino-tetraiodomercuriate,** $Cu_2HgI_4.3\frac{1}{2}NH_3$, and brown **cuprous octammino-tetraiodomercuriate,** $Cu_2HgI_4.8NH_3$, by the action of the gas on the dried salt.

M. Bellati and R. Romanese also report **cuprous hexaiodomercuriate,** $4CuI.HgI_2$, or Cu_4HgI_6.

In attempting to make cuprous iodomercuriates F. Anderlini obtained yellow crystals of two products which were too unstable for analysis, but he obtained compounds with $HgI_2 : CuI : NH_3$ in the approximate ratios 3 : 1 : 6, 2 : 1 : 3, 2 : 1 : 4, and 1 : 1 : 2. The compound **cuprous diammino-triiodomercuriate,** $CuHgI_3.2NH_3$, was obtained by adding ammonium sulphite to a soln. of a copper salt, heating nearly to boiling, and adding a soln. of potassium mercuric iodide. Mercury separates out, and the soln. is kept at 50° until it is clear. The hot liquid is filtered, and on cooling brownish-yellow crystals separate out; these are washed with aq. alcohol and dried in a desiccator over a mixture of calcium oxide and potassium hydroxide—not calcium chloride. The crystals gradually redden on exposure to air; they melt with decomposition, below 100°; they are decomposed by water and alcohol; they become blue, forming $CuHgI_4.2NH_3$ by the action of ammonia in moist air; and they are soluble in a warm soln. of ammonium sulphite, but lose their colour and give off ammonia. F. Anderlini prepared **cuprous triammino-pentaiodo-dimercuriate,** $CuHg_2I_5.3NH_3$, by dissolving the mercuric diammino-iodide, $HgI_2.2NH_3$, in a soln. of ammonium sulphite, and adding an ammoniacal soln. of cupric iodide to the hot soln. When the blue liquid is kept at 60°–70°, it gradually becomes yellow, and yellow crystals of the triammino-compound are deposited on cooling. The dry compound becomes red on exposure to air; it is decomposed by prolonged washing with water, and also by absolute alcohol but more slowly than by water. **Cuprous tetrammino-pentaiodo-dimercuriate,** $CuHg_2I_5.4NH_3$, is obtained if in preparing the triammino-compound, the soln. are mixed cold, and warmed to 50° until the precipitate has redissolved. The bright yellowish-green crystals behave like the triammino-compound when exposed to air, to water, and to alcohol. F. Anderlini also reported a compound, **cuprous hexammino-hexaiodo-trimercuriate,** by a process resembling that for $CuHg_2I_5.4NH_3$, but using strongly ammoniacal soln. The analyses do not show whether the green plates have the composition $CuHg_3I_6.5NH_3$ or $6NH_3$. Two cupric ammino-iodomercuriates have been reported by S. M. Jörgensen and F. Anderlini, namely, 2 : 1 : 4 and 1 : 1 : 4. S. M. Jörgensen made **cupric tetrammino-tetraiodo-mercuriate,** $HgI_2.CuI_2.4NH_3$, or $CuHgI_4.4NH_3$, by the action of alcohol on a mixture of cupric tetrammino-tetraiodide, $CuI_4.4NH_3$, and mercury for some hours at ordinary temp. The blue mass of crystals can be purified by recrystallization from hot ammoniacal alcohol. He also obtained the same compound by slowly cooling a hot soln. of cupric amminosulphate and potassium iodomercuriate, and washing the product, first with water and then with ammoniacal alcohol. F. Anderlini also prepared this compound by cooling a warm ammoniacal soln. of $CuHg_2I_6.4NH_3$. The prismatic crystals of $CuHgI_4.4NH_3$ are an intensely blue colour; they are gradually decomposed at 135°; they are easily decomposed by water and by acids; when boiled with zinc and water iodine goes quantitatively into soln. and copper, mercury, and the excess of zinc remain; they dissolve in conc. soln. of neutral ammonium salts—chloride, bromide, sulphate, etc.—with the evolution of ammonia; and the soln. on cooling deposits green crystals of **cupric tetrammino-hexaiododimercuriate,** $CuI_2.2HgI_2.4NH_3$, or $CuHg_2I_6.4NH_3$, which gives the original compound, $CuI_2.HgI_2.2NH_3$, when treated with ammonia. S. M. Jörgensen previously prepared the compound $CuI_2.2HgI_2.4NH_3$ by shaking the blue soln. obtained by digesting at 30° cuprous iodide with an alcoholic soln. of iodine—$CuI+9I$—with mercury; the green liquid is decanted from the mercurous iodide, and warmed with alcoholic ammonia. The resulting blue liquid furnishes dark green crystals of the compound in question. S. M. Jörgensen made the same compound by mixing warm soln. of potassium iodomercuriate and cupric ammino sulphate; the crystals which separate on cooling were rapidly washed with water, and dried in darkness in vacuo over calcium chloride. The dark green crystals can be kept in sealed vessels, but in air they lose iodine and ammonia; they are

sensitive to light; they lose ammonia and mercuric iodide when heated to 135°; by prolonged washing with water they form a mixture of cuprous and mercuric iodides, and also when treated with dil. acids; they are soluble in an alcoholic soln. of acetic acid; they behave like $CuI_2.HgI_2.4NH_3$ towards zinc and water; and they form $CuI_2.HgI_2.4NH_3$ when warmed with an excess of ammonia—some cupric iodide passes into soln.

H. W. B. Roozeboom and A. Steger [11] have studied the effect of temp. on mixtures of silver and mercuric iodides. When the liquid mixture solidifies, mixed crystals are formed in all proportions excepting for the gap between 5 and 20 mol. per cent. of silver iodide—the mixed crystals with less than 5 mol. per cent. of silver iodide are of the rhombic mercuric iodide type; and (β), those containing 20 to 100 mol. per cent. of silver iodide are of the regular silver iodide type. Liquid mixtures with between 5 and 20 mol. per cent. of silver iodide solidify at 242° into a mixture of the two types of mixed crystals; the gap is wider at lower temp. being from 2 to 35 mol. per cent. of silver iodide at 132·5°, as is illustrated in Fig. 33. The mixed crystals β, containing between 40 and 90 mol. per cent. of silver iodide, undergo a change, the maximum temp. of which is 158°, in a mixture with 66 mol. per cent. of silver iodide. Apparently the mixed crystals (β) are then changed into the compound $HgI_2.2AgI$, and the maximum temp. of this change is strictly analogous to the maximum f.p. of a pure compound.

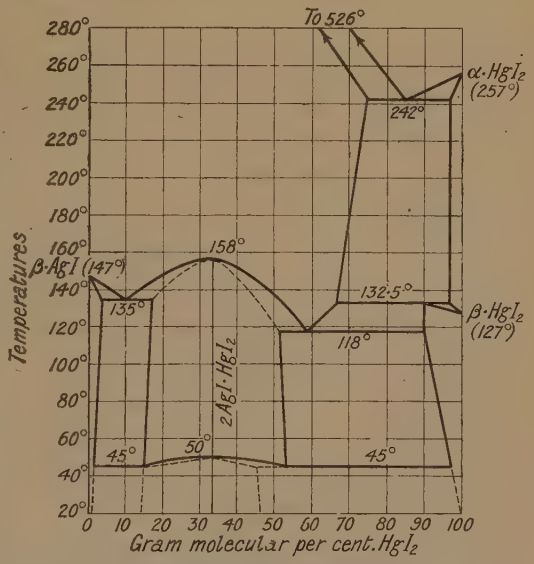

FIG. 33.—Equilibrium Diagram of Mixtures of Silver and Mercuric Iodides.

In the mixed crystals (β) containing either more mercuric iodide or more silver iodide than is required for the compound, the temp. of change is lowered, on the silver iodide side to the point 135°, 90 mol. per cent., on the mercuric iodide side to the point 118°, 40 mol. per cent., these two being analogous to eutectic points on freezing curves. On neither side of the maximum, however, is the pure compound formed; according to the side, there is an admixture of silver iodide or mercuric iodide. A further complication has been detected at low temp., inasmuch as the above-mentioned double salt undergoes a transformation at 50°–45°, the colour changing from red to yellow. This has been discussed by R. E. Liesegang.

The evidence as to the formation of **silver tetraiodomercuriate,** $2AgI.HgI_2$, or Ag_2HgI_4, is not very definite. H. Wegelius and S. Kilpi prepared it by treating freshly precipitated well-washed silver chloride with potassium iodomercuriate; and E. Meusel, by treating a soln. of silver nitrate with potassium iodomercuriate. E. Meusel, however, said that the yellow precipitate he obtained is not a compound. L. Cramer prepared silver iodomercuriate as an emulsion by adding silver nitrate and potassium iodide to an emulsion of mercuric iodide in gum arabic. H. Rebenstorff crystallized the compound from a hot soln. of mercuric nitrate. M. Bellati and R. Romanese found the sp. gr. to be 5·9984 at 0°, when the value calculated from the law of mixtures is 6·038. E. Meusel and R. Böttger showed that when the yellow precipitate of mercuric and silver iodides is heated under water it becomes intensely red, and the yellow colour is restored on cooling; and they stated that

mechanical mixtures of the two insoluble iodides present a similar phenomenon. M. Bellati and R. Romanese studied the remarkable colour changes which occur when mixtures of mercuric and silver iodides are heated; the compound Ag_2HgI_4 was found to be canary-yellow at ordinary temp.; orange at 47·5°; orange-red at 48·5°; and bright red at a higher temp. The reversible colour change which occurs in the neighbourhood of 50° was supposed by A. E. Baur to be due to the decomposition of the complex salt, Ag_2HgI_4, and not to dimorphism, because he observed no break in the e.m.f. curve up to 53°. H. Wegelius and S. Kilpi drew the opposite conclusion. They found that after adding silver chloride to the liquid, the canary-yellow precipitate which changes to a blood-red at 50°, gradually passes into the pale yellow colour of silver iodide as the proportion of silver chloride is increased. If so little silver chloride is present that the soln. after the formation of the canary-yellow precipitate still contains a considerable proportion of mercuric iodide, the transformation can be frequently repeated without forming solid silver iodide. H. W. B. Roozeboom places the transition point at 45°; and H. Rebenstorff says that both modifications can exist in presence of one another between about 33° and 45°; and he devised a colour thermoscope based on this transformation. According to M. Bellati and R. Romanese, the thermal expansion increases regularly up to 40°, so that the volume v, at the temp. $\theta°$, is $v=1+0·000095537\theta$; between 45° and 50°, the volume changes are irregular owing to changes in the internal structure; and above 51°, the thermal expansion is again regular when $v=1·006165+0·0000881102\theta$. They also find that the thermal expansion of the compound is greater than would be the case if it were a mechanical mixture. They give the mean sp. ht. between $\theta_1°$ and $\theta_2°$ as $0·035648+0·00057835(\theta_1+\theta_2)-0·0000052621(\theta_1^2+\theta_1\theta_2+\theta_2^2)$; the true sp. ht. at $\theta°$, as $0·035648+0·00115567\theta-0·000015786\theta^2$; the amount of heat required to raise the temp. from 0° to $\theta°$ as $1·58600+0·0613035\theta$; the sp. ht. at 51° as 0·06130 which they say is constant; and the heat of transformation at 50° as 2·0807 cals., and at 41°, 2·0283 cals. Alcohol gradually decomposes Ag_2HgI_4 into mercuric iodide.

M. Bellati and R. Romanese also cited evidence to show the formation of $HgI_2.AgI$, and $HgI_2.2AgI$. They showed that the sp. gr., thermal expansion, sp. ht., and heat of transformation of $HgI_2.3AgI$ from the values for $HgI_2.2AgI$ and AgI agree with the assumption that $HgI_2.3AgI$ is a mixture. Similar evidence indicates that $HgI_2.AgI$ and $HgI_2.2AgI$ are compounds. Thus, the sp. gr. of *silver triiodomercuriate*, $AgHgI_3$, is 5·9302 at 0°, when the value calculated from the mixture law is 5·990; the thermal expansion is much greater than corresponds with the mixture law, being $v=1+0·000065689\theta$ for values of θ between 0° and 40°; for values of θ over 50°, $v=1·003500+0·0000840056\theta$; and there is a great irregularity between 40° and 52° as is the case with $HgI_2.2AgI$. The salt $HgI_2.AgI$ shows similar colour changes to those presented by $HgI_2.2AgI$. The mean sp. ht. between θ_1 and θ_2 is $0·054404+0·00079681(\theta_1+\theta_2)$; the true sp. ht. at $\theta°$ is $0·054404+0·0001593624\theta$; and the heat of transformation at 49°, 1·7525, and at 41°, 1·7323.

M. C. Lea prepared a compound or mixture with a composition approximating to *silver dichlorodiiodomercuriate*, $2AgCl.HgI_2$, by mixing moist and freshly precipitated silver chloride and mercuric iodide; and by the action of eq. quantities of potassium iodide, mercuric chloride, and silver nitrate. The yellow powder gradually reddens when heated above 38°, and the scarlet-red colour is a maximum at 60°; the original colour is restored on cooling. The colour of the product is darkened in sunlight, and the original colour is restored in darkness. Consequently, M. C. Lea concludes that a compound is here in question.

According to P. F. G. Boullay,[12] when a hot aq. soln. of calcium iodide, sat. with mercuric iodide, is cooled, some mercuric iodide is deposited, and the mother liquid, on evaporation, furnishes crystals of what is thought to be *calcium hexaiododimercuriate*, $2HgI_2.CaI_2$, or $CaHg_2I_6$; the crystals are decomposed by water, furnishing red mercuric iodide and a liquid which leaves a yellow mass on

evaporation. J. B. Berthemot also obtained yellow needles from the soln. obtained by boiling mercuric iodide with calcium oxide and alcohol. A. G. Duboin alternately dissolved calcium and mercuric iodides in water up to saturation when a soln. with the molar composition, $CaI_2+1{\cdot}3HgI_2+12{\cdot}3H_2O$, was produced—the sp. gr. was 2·89 at 15·9°. By cooling this soln., crystals of **octohydrated calcium tetraiodomercuriate,** $CaI_2.HgI_2.8H_2O$, or $CaHgI_4.8H_2O$, are formed; similar crystals were obtained by evaporating a soln. containing at 9·5°, 21·39–21·66 per cent. of water, 3·97 per cent. of calcium, 21·57–21·84 per cent. of mercury, and 52·8 per cent. of iodine. The yellow needle-like crystals have a sp. gr. 3·258 to 3·337 at 0°; they are very deliquescent; they dissolve in water without decomposition; they also dissolve in many organic solvents without decomposition—*e.g.* methyl-, ethyl-, amyl-, butyl-, and isobutyl-alcohols; in allyl iodide, acetone, acetic acid, ethyl oxalate, aniline, they are sparingly soluble in nitrobenzene; and they are insoluble in chloroform, carbon tetrachloride, ethyl iodide, ethylene iodide, benzene, monochlorobenzene, and toluene. If mercuric iodide be dissolved in the mother liquid remaining after the separation of the above described crystals, and the soln. cooled to 0°, A. G. Duboin found that small crystals of **octohydrated calcium dodecaiodopentamercuriate,** $CaI_2.5HgI_2.8H_2O$, or $CaHg_5I_{12}.8H_2O$, which have a sp. gr. of 4·69 (0°), are formed. They are less deliquescent than those of $HgI_2.CaI_2.8H_2O$; they are decomposed by water and by methyl-, ethyl-, and amyl-alcohols, by glycerol, aldehyde, acetone, and acetic acid, with the formation of red mercuric iodide; they are decomposed slowly by nitrobenzene and ethyl oxalate; and they are insoluble in monochlorobenzene, toluene, ethylene bromide, and chloroform. If the soln. just mentioned be further cooled below 0°, elongated prisms are also formed. These crystals have the composition **calcium tetradecaiodotetramercuriate,** $3CaI_2.4HgI_2.24H_2O$, and sp. gr. 3·56–3·66 at 0°; they dissolve in water with the separation of mercuric iodide; they readily dissolve in methyl-, ethyl-, amyl-, butyl-, and isobutyl-alcohols, glycerol, ethyl acetate, methyl- and isobutyl propionates, allyl iodide, aldehyde, acetone, aniline, and ethyl oxalate; they are very sparingly soluble in nitrobenzene; and insoluble in monochlorobenzene, toluene, ethylene bromide, ethyl iodide, chloroform, carbon tetrachloride, etc.

According to P. F. G. Boullay, a soln. of strontium iodide, sat. hot with mercuric iodide, deposits part of the latter on cooling, and when the mother liquid is evaporated, it gives crystals of what was thought to be *strontium hexaiododimercuriate*, $SrI_2.2HgI_2$, or $SrHg_2I_6$, and which are decomposed by heat, or by treatment with water. J. B. Berthemot also made yellow crystals from the soln. obtained by boiling mercuric iodide with strontia water. The composition of these crystals has not been definitely established. A. G. Duboin alternately dissolved strontium and mercuric iodides in water at 16·5° until the soln. was saturated; the composition of the soln. was $SrI_2+1{\cdot}24HgI_2+18{\cdot}09H_2O$, and its sp. gr. 2·5; when strongly cooled, iridescent plates of **octohydrated strontium dodecaiodopentamercuriate,** $SrI_2.5HgI_2.8H_2O$, or $SrHg_5I_{12}.8H_2O$, and sp. gr. 4·66 (0°), separated out. The same salt was obtained in quantity by cooling a soln. of strontium iodide sat. with mercuric iodide at 70°. A second salt, **octohydrated strontium tetraiodomercuriate,** $SrI_2.HgI_2.8H_2O$, or $SrHgI_4.8H_2O$, was obtained in long prismatic crystals by the slow evaporation of a soln. with the composition: strontium, 7·85 per cent.; mercury, 21·22 per cent.; iodine, 50·44 per cent.; water, 20·49 per cent. The crystals have a sp. gr. 3·22 to 3·36 at 0°. The properties resemble those of the corresponding calcium salt.

P. F. G. Boullay prepared what was assumed to be *barium hexaiododimercuriate*, $BaI_2.2HgI_2$, by a process analogous to that employed for the strontium salt. According to A. G. Duboin, a soln. saturated with both barium and mercuric iodides has the composition $BaI_2+1{\cdot}33HgI_2+7{\cdot}76H_2O$, and sp. gr. 2·76 at 23·5°. When this soln. is sat. at 70° with mercuric iodide, and cooled, it furnishes small crystals of **octohydrated barium dodecaiodopentamercuriate,** $BaI_2.5HgI_2$.

$8H_2O$, or $BaHg_5I_{12}.8H_2O$, of sp. gr. 4·63 at 0°. This salt resembles the corresponding salts of strontium and calcium. A. G. Duboin evaporated a soln. containing $1·07BaI_2+HgI_2+9·71H_2O$ in a desiccator over sulphuric acid, and obtained prismatic deliquescent crystals of **hexadecahydrated barium hexadecaiodopentamercuriate,** $3BaI_2.5HgI_2.16H_2O$, or $Ba_3Hg_5I_{16}.16H_2O$, with a sp. gr. 4·06. Prismatic crystals of **hexadecahydrated barium decaiodotrimercuriate,** $2BaI_2.3HgI_2.16H_2O$, can be obtained by cooling a soln. containing $BaI_2+1·3HgI_2+10·4H_2O$. Similar crystals can also be obtained from the mother liquid remaining after the separation of $BaI_2.HgI_2.8H_2O$. These crystals have a sp. gr. of 4 at 0°. If a soln. of the composition 12·45 per cent. barium, 22·53 per cent. mercury, 51·68 per cent. iodine, and 13·34 per cent. water, be evaporated in dry air at a summer heat, large flattened crystals of **pentahydrated barium tetraiodomercuriate,** $HgI_2.BaI_2.5H_2O$, or $BaHgI_4.5H_2O$, and sp. gr. 4 at 0°, are obtained. H. Ley and G. Wiegner, and W. Peters prepared **barium octammino-tetraiodomercuriate,** $BaHgI_4.8NH_3$, from its constituents by the action of the gas on the dried salt. The absorption is rapid at 20°.

M. Herder proposed a soln. of barium mercuric iodide as a reagent for alkaloids; and C. Rohrbach prepared a soln. of barium and mercuric iodides—*Rohrbach's solution*—of sp. gr. 3·575 to 3·588, for separating heavy minerals.

100 grms. of barium iodide, and 130 grms. of mercuric iodide are mixed in a dry flask; 20 c.c. of water are added, and the mixture is continually agitated while being heated to 150° or 200° on an oil-bath. The soln. is then allowed to evaporate on a water-bath until a fragment of epidote floats thereon; the soln. is then allowed to cool, when a double salt is deposited. This is allowed to settle in a tall beaker, and the clear liquid decanted. Filtration is not recommended. The soln. is decomposed when diluted with water, and it is therefore diluted with a more dil. soln. Its properties are similar to Thoulet's soln. Rohrbach's soln. is not changed by carbon dioxide or by carbonates—*e.g.* calcite or chalk. The soln. boils at 145°. The refractive index of a soln. of sp. gr. 3·564 is 1·7755 for the *C*-line; 1·7932 for the *D*-line; 1·8265 for the *E*-line; and 1·8488 for the *F*-line; the dispersion $\mu_F-\mu_C$ is 0·0736, and $(\mu_F-\mu_C)/\mu_C=0·0409$. E. Clerici has measured the viscosity of the soln.

According to P. F. G. Boullay,[13] a hot soln. of magnesium iodide sat. with mercuric iodide deposits a portion of the latter on cooling, and the mother liquid yields greenish-yellow needles on evaporation. These crystals are thought to be **magnesium hexaiododimercuriate,** $MgI_2.2HgI_2$. They are decomposed by water into red mercuric iodide, and, according to P. F. G. Boullay, a soln. of probably magnesium tetraiodomercuriate, $HgI_2.MgI_2$. According to A. G. Duboin, a soln. of the composition $MgI_2+1·29+11·06H_2O$, and sp. gr. 2·92 at 17·8°, furnishes first a crop of crystals of **heptahydrated magnesium hexaiododimercuriate,** $MgI_2.2HgI_2.7H_2O$, or $MgHg_2I_6.7H_2O$, sp. gr. 3·8 (0°), and properties like the corresponding calcium salt; and then a crop of deliquescent octahedra of **enneahydrated magnesium tetraiodomercuriate,** $MgI_2.HgI_2.9H_2O$, or $MgHgI_4.9H_2O$, sp. gr. 2·9. A. G. Duboin also reports crystals of $3MgI_2.5HgI_2.xH_2O$, analogous with the corresponding barium salt. F. Calzolari and U. Tagliavini prepared crystals of a complex of $HgI_2.MgI_2.10H_2O$ with hexamethylenetetramine.

According to P. A. von Bonsdorff, when an aq. soln. of zinc iodide, sat. with mercuric iodide, is evaporated over sulphuric acid in a desiccator, a first crop of crystals of mercuric iodide is followed by yellow deliquescent prisms of the double iodide; P. F. G. Boullay also reported that a hot aq. soln. of a mol of zinc iodide dissolves not quite two mols of mercuric iodide; the soln. deposits part of the last-named salt on cooling, and still more when diluted with water. According to A. G. Duboin, the crystals successively deposited from mixed soln. of mercuric and zinc iodides form a complete series of mixed crystals, and he believed that the crystals of **zinc tetraiodomercuriate,** $ZnI_2.HgI_2$, previously described, are isomorphous mixtures and not definite compounds. A soln. saturated at 14·5 with both salts has the composition $HgI_2+1·87ZnI_2+16·33H_2O$, and sp. gr. 2·82. Similar remarks apply also to the crystals of **cadmium tetraiodomercuriate,**

$CdI_2.HgI_2$, and **cadmium octoiodotrimercuriate,** $CdI_2.3HgI_2$, prepared as pale yellow crystals by J. B. Berthemot from the soln. obtained by triturating moist mercuric iodide with cadmium filings; and by F. W. Clarke and E. A. Kebler from a hot soln. of mercuric iodide in cadmium iodide. C. Sandonnini also obtained crystals containing all proportions of cadmium and mercuric iodides from fused mixtures of the component salts, Fig. 34. The transition temp. of mercuric iodide is lowered from 128° to 105° when 30 molar per cent. of cadmium iodide is present. F. Ephraim and P. Mosimann prepared pale yellow octahedra or cubes of **zinc mercuric tetramminotetraiodide,** $[Zn(NH_3)_4]HgI_4$. They also made **cadmium mercuric tetramminotetraiodide,** $[Cd(NH_3]_4]HgI_4.4H_2O$, and **cadmium mercuric hexamminotetraiodide,** $[Cd(NH_3)_6]HgI_4.6H_2O$, in conc. ammoniacal soln. These salts can also be regarded as zinc or cadmium amminotetraiodomercuriates. H. Ley and G. Wiegner, and W. Peters prepared $CdHgI_4.6NH_3$ by exposing the product regarded as $CdHgI_4$ to the action of ammonia gas.

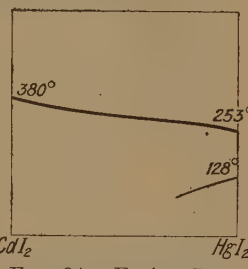

FIG. 34.—Fusion Curve of Binary Mixtures of Cadmium and Mercuric Iodides.

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§ 27. The Sulphides of Mercury

Our knowledge of cinnabar probably goes as far back as that of mercury. Theophrastus, in his Περὶ Λίθων, written about 300 B.C., mentioned two kinds of κιννάβαρ—the natural and the fictitious. The former is analogous with cinnabar, the ore from which mercury is extracted ; the latter appears to have been a powdered and levigated red sand obtained near Ephesus. Pliny, in his *Historia naturalis*, written at the beginning of our era, also speaks of the confusion between the mineral cinnabar, which he called *minium*, and *Indian cinnabar*, the dried juice or resin known as dragon's blood—*sanies draconis*—probably obtained from the calamus palm, or *Pterocarpus draco*. Pliny's contemporary, Dioscorides, also

called cinnabar *ἄμμιον*. Pliny's term minium is now reserved for red-lead. The subsequent history has been well outlined by H. Kopp, and M. Berthelot. The artificial preparation of red mercury sulphide—called *usifur*—was described by Geber in his *Summa perfectionis magisterii*, written about the thirteenth century; and, about the same time, Albertus Magnus, in his *Compositum et compositis*, showed that cinnabar, or *lapis rubeus*, is a compound of mercury and sulphur, because "when a mixture of mercury and sulphur is sublimed, a brilliant red powder of cinnabar is produced." This conclusion was repeated by many later writers[1]—A. Libavius, J. Kunckel, G. E. Stahl, H. Boerhaave, J. J. Becher, N. Lemery, etc. J. S. Carl showed the identity of natural, artificial, and antimonial cinnabar, and stated that the composition was six parts of mercury and one of sulphur. Black mercuric sulphide was prepared near the beginning of the eighteenth century by W. Harris, and Turquet de Mayerne by triturating mercury and sulphur, and the product was variously called *æthiops mineralis*, *æthiops mercuralis*, *æthiops Turqueti* or *æthiops Harrisii*, *mineralis mohr*, *Quecksilbermohr*, or *æthiops empyros* or *apyros*, according as the sulphur employed was melted or not. In 1752, H. Ludolf prepared black mercuric sulphide by the action of a soln. of calcium sulphide on mercury or mercuric oxide; five years later, J. C. Jacobi used a soln. of alkali sulphide, and the product was called *pulvis hypnoticus*, or *narcoticus Krielii*, after D. S. C. Kriel, who recommended it as a medicine. In 1687, G. Schultz made cinnabar in the wet way by treating mercury with a soln. of ammonium sulphide, *spiritus fumans Boylei*; and a similar process was used by F. Hoffmann, and J. C. Wiegleb. A. Baumé showed that this sulphide soln. converts the black sulphide as well as mercury itself into cinnabar; and J. Senebier, that hydrogen sulphide acts slowly with the same result. The black and red forms of mercuric sulphide puzzled the early chemists. G. E. Stahl assumed that the black form contained more sulphur than the red one; P. J. Macquer, A. F. de Fourcroy, and L. N. Vauquelin assumed that the sulphur in the black form was less intimately associated with the mercury than in the red form; A. F. de Fourcroy also postulated that both compounds were sulphuretted mercury oxides, but that the red form was more oxidized than the black one; C. L. Berthollet assumed that cinnabar is a true sulphide, and that the black form is a hydrosulphide; C. F. Bucholz suggested the converse of Berthollet's hypothesis; J. B. Trommsdorff assumed that cinnabar is a sulphide, and that the black sulphide is a sulphuretted oxide. J. L. Proust, C. F. Buchloz, and J. M. Séguin showed the sulphides are free from oxygen; and in 1833 J. N. von Fuchs explained the difference by assuming that the black sulphide is amorphous, and that the red sulphide is crystalline.

The analyses of J. L. Proust, J. M. Séguin, N. J. B. G. Guibourt, N. G. Sefström, and O. L. Erdmann and R. F. Marchand correspond with the formula HgS. Cinnabar has been analyzed by A. Bealey, R. Varet, M. H. Klaproth, H. Müller, F. Pisani, and C. F. Rammelsberg; and metacinnabarite by J. Petersen, G. Cesaro, J. D. Whitney and G. E. Moore, F. A. Genth, W. H. Melville and W. Lindgren, R. Varet, O. Schumann, A. Schrauf, etc. The occurrence of metacinnabarite has also been discussed by G. Kroupa,[2] J. A. Krenner, W. H. Melville, and A. Schrauf. It was formerly believed that the ores of mercury were formed in nature by sublimation; and that the uniformity in the characteristics of most of the deposits points to a common origin. The presence of accessory minerals—calcite, opal, barite, etc.—is opposed to the sublimation hypothesis, and since hot springs and volcanic products are associated with most of the deposits, it is assumed that they have been formed by the agency of hot springs. At Almaden (Spain), Idria (Austria), and Nikitowka (Russia), the evidences of volcanic agents are not so marked, but since the characteristic mineral associations are the same, the latter theory still holds good. F. W. Clarke assumes that cinnabar was probably deposited from ascending soln. because such soln. are alkaline, and that metacinnabarite was deposited by descending soln. because of their acidity—the acid being derived from the oxidation of pyrites.

According to A. L. Orlowsky,[3] with the exception of copper, mercury possesses a greater affinity for sulphur than any other metal; E. Schürmann, however, estimated the affinity of mercury for sulphur to be smaller than that of palladium, but greater than that for silver or copper; and O. Schumann said that the affinity of mercury for sulphur is smaller than that of barium, and nearly the same as that of the metal for oxygen. M. Berthelot observed no reaction between dry hydrogen sulphide and mercury at 100°. It is somewhat doubtful if all the reports of the preparation of **mercurous sulphide,** Hg_2S, can be substantiated, although it appears to be possible to prepare it at temp. below 0°.

According to H. V. Regnault, J. J. Berzelius, and W. T. Brande, mercurous sulphide is obtained by the action of hydrogen sulphide on a soln. of a mercurous salt, though N. J. B. G. Guibourt stated that the product is only a mixture of mercury and mercuric sulphide. C. Barfoed obtained similar results, and E. Weinschenk showed that a similar mixture is obtained by the action of compressed hydrogen sulphide on mercurous chloride. On the other hand, U. Antony and Q. Sestini probably obtained mercurous sulphide by the action of a mixture of hydrogen sulphide and carbon dioxide on mercurous chloride cooled by a freezing mixture below −10°. K. Brückner, and A. Violi also obtained what they regarded as mercurous sulphide by heating mercurous sulphate with sulphur; and C. Baskerville, by leaving mercury (10 grms.) in contact with 99·65 per cent. sulphuric acid (50 grms.) in a closed flask shut off from the direct action of sunlight. After about five years the black product was washed rapidly by decantation with much water, then with 95 per cent. alcohol, and dried at 110°.

According to U. Antony and Q. Sestini, the black or brownish-black powder is quite stable at −18°, but above 0°, it readily decomposes into mercury and mercuric sulphide. C. Baskerville found that when heated in a closed tube it becomes white —probably owing to oxidation—then yellow, and it finally melts to a dark orange liquid which on cooling forms white mercurous sulphate. W. Hittorf said that what was thought to be mercurous sulphide conducts an electric current like a metal, and W. Skey showed that it is more electropositive than silver towards a soln. of sodium chloride, and, when used as the negative pole of a cell, it is desulphurized. According to U. Antony and Q. Sestini, hydrogen chloride mixed with carbon dioxide rapidly converts mercurous sulphide into hydrogen sulphide and mercurous chloride; mercuric sulphide remains unchanged by this treatment. Dil. hydrochloric and dil. nitric acids do not act on mercurous sulphide below 0°, but more conc. nitric acid has a slight action; at a higher temp., these acids react as they would on a mixture of mercuric sulphide and mercury; fuming nitric acid rapidly oxidizes mercurous sulphide, forming mercuric nitrate and sulphur, which is partly oxidized to sulphuric acid. Ammonium sulphide or hydroxide, and alkali hydroxides have no action; sodium, or better, potassium sulphide, rapidly dissolves mercurous sulphide, forming a clear liquid which, as the temp. rises, becomes turbid owing to the separation of finely divided mercury, and the formation of mercuric sulphide.

There are three crystalline **mercuric sulphides,** HgS—the red form, α-HgS, corresponding with cinnabar or vermilion; the black cubic form, corresponding with metacinnabarite, α'-HgS; and a deep red hexagonal form, β-HgS, not found in nature. In addition, there is an amorphous or colloidal mercuric sulphide. Cinnabar is the stable form of mercuric sulphide at all temp. up to its sublimation point, about 580°; it is readily formed by the action of soluble alkali sulphides on the amorphous black sulphide—say, by heating the latter with a conc. soln. of ammonium sulphide in a sealed tube at 100°, when the colour becomes red in a short time, but the action is continued for about 24 hrs. to ensure a complete conversion. According to E. T. Allen and J. L. Crenshaw,[4] black amorphous sulphide is always the first product of the action of alkali sulphides on mercuric salts, but cinnabar only is obtained when the precipitate is digested with alkaline soln.; no metacinnabarite was ever obtained under this condition. According to A. Christensen, when

mercuric salts—the oxalate, acetate, sulphate, chloride, iodide, etc.—are heated with an aq. soln. of ammonium monosulphide, the soln. become yellow owing to the partial liberation of sulphur, with the formation of ammonium polysulphide, and the precipitate is a mixture of mercury and mercuric sulphide. Yellow mercuric oxide also imparts the yellow colour to the soln. of ammonium sulphide, but the sulphur slowly returns to the solid, forming vermilion. Mercuric cyanide very quickly forms vermilion. Mercuric sulphide does not yield sulphur to ammonium sulphide soln., so that the liberation of sulphur occurs when the mercuric salt and ammonium sulphide interact. Sodium sulphide behaves like ammonium sulphide, but the separation of sulphur is less marked. B. S. Neuhausen studied the precipitation of mercuric sulphide from cyanide soln., and concluded that reactions at low conc. are between mols. or complex ions.

According to E. T. Allen and J. L. Crenshaw, the product of the action of soluble thiosulphates on mercuric salts depends on the ratio of the two salts in the soln., and also on the conc. The results are summarized in Fig. 35, with reference to 10 per cent. with about 2 per cent. of sodium chloride added, because the decomposition of sodium mercuric chloride proceeds more slowly than that of soln. of mercuric chloride and better crystals are produced. The line *AB* includes all soln. with the ratio $HgCl_2 : Na_2S_2O_3 = 3 : 2$, and soln. above that line contain more mercuric chloride; these soln. all furnish white *mercuric dichlorodisulphide*, $HgCl_2.2HgS$; the reaction is symbolized: $3HgCl_2 + 2Na_2S_2O_3 + 2H_2O = HgCl_2.2HgS + 4NaCl + 2H_2SO_4$. Soln. corresponding with the line *AC* contain $HgCl_2 : Na_2S_2O_3$ in the ratio 1 : 1, and soln. in the region between *AB* and *AC* furnish a mixture of mercuric thiochloride, and black mercuric sulphide: $HgCl_2 + Na_2S_2O_3 + H_2O = 2NaCl + H_2SO_4 + HgS$ (black).

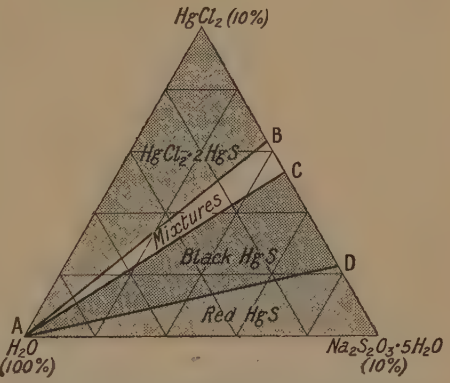

FIG. 35.—The Action of Sodium Thiosulphate on Mercuric Chloride Solutions.

All soln. lying in the region between *AC* and *AD* precipitate at the beginning black mercuric sulphide, though later a red precipitate may be obtained. The line *AD* includes soln. in which the ratio $HgCl_2 : Na_2S_2O_3$ is as 1 : 4. Below *AD*, the principal reaction is $HgCl_2 + 4Na_2S_2O_3 = 2NaCl + 3Na_2SO_4 + 4S + HgS$. The mercuric sulphide precipitated at the beginning is a deep red modification which is not cinnabar; the precipitation of this compound continues until the dilution of the supernatant liquid has fallen to about one per cent. of mercuric chloride, when the black crystalline form appears. The reaction between sodium thiosulphate and sodium mercuric chloride renders the soln. slightly acid, a condition essential for the production of metacinnabarite. A. L. T. Mösveld also found that the metacinnabarite form is precipitated from faintly acid soln., and the cinnabar form from neutral or faintly alkaline soln.

Under the name *vermilion*, the red sulphide is employed as a pigment. The Chinese used it for colouring ink, paper, tapers, etc., and many temples in China are painted with the same colour; it is regarded by them as a lucky colour. Cinnabar is not used as a pigment because the impurities affect the colour. Vermilion is made by wet and dry processes. The dry processes depend on the preparation of the black sulphide, and its subsequent conversion into the red variety; and cinnabar is made by subliming a mixture of sulphur with mercury, mercury oxide, or mercury sulphate. According to H. Boerhaave, when 5–6 parts of mercury are added to one part of molten sulphur, and the mixture heated, with constant stirring until the sulphur thickens, the two elements unite with violent

crackling, and the evolution of heat and light. The resulting mass is blackish-red, and appears to be a mixture of black and red mercuric sulphides with some uncombined sulphur and mercury. When this product is powdered, mixed with a little sulphur, and heated in a glass flask with a loose-fitting charcoal stopper, a sublimate of cinnabar is obtained; the more volatile free sulphur escapes, and the foreign metals, as sulphides, remain in the flask. If the upper part of the flask is too hot, some cinnabar is lost by volatilization. F. Pilz recommended washing the vermilion with a boiling soln. of potassium carbonate.

L. Gmelin described the old method of preparation formerly employed at Amsterdam, and this is very like that just indicated. E. Mitscherlich described the old method employed at Idria, where the sulphur and mercury are agitated in rotating cylinders for some hours so as to furnish a brown powder. The mixture is heated in covered cast-iron cylindrical retorts with iron capitals; these are replaced by stoneware capitals with the beaks connected by a tube and receiver. The best vermilion collects in the capitals. This is removed and washed first with boiling sodium hydroxide, then water; the washed powder is then dried. Anonymous writers have described the Chinese method of preparation. This resembles in many respects that indicated above. The vermilion prepared by the above processes, said E. Wehrle, has a yellow tinge, and he claimed that if about one per cent. of antimony sulphide be added to the mixture of sulphur and mercury before sublimation, and the finely ground sublimate be boiled a number of times with a soln. of liver of sulphur, digested with hydrochloric acid, and afterwards washed and dried, it assumes the fine scarlet colour of the Chinese vermilion. No antimony can be detected in the final product.

C. Doelter made crystals of cinnabar by heating mercury with hydrogen sulphide in a sealed tube at 70°–90° for several days; but if mercury be heated with an aq. soln. of hydrogen sulphide on a water-bath, a mixture of red and black sulphides is formed. According to F. Fouqué and A. M. Lévy, cinnabar was made by J. Durocher by the action of hydrogen sulphide on red-hot mercuric chloride, and by H. St. C. Deville and H. Debray, by heating the black precipitated sulphide with hydrochloric acid in a sealed tube at 100°. W. Spring obtained the red sulphide by strongly compressing a mixture of sulphur and mercury; and he also obtained red streaks by rubbing the black powder with an agate pestle and mortar.

The wet processes for making vermilion depend on the fact that alkali sulphides convert black into red mercuric sulphide. F. Hoffmann digested mercury with ammonium polysulphide, Boyle's spirit of sulphur, and obtained the red sulphide in a few days. A. Baumé obtained similar results with mercuric nitrate and Boyle's spirit of sulphur, but mercuric chloride did not work so well. J. L. Proust found that the black precipitated sulphide turns red slowly at ordinary temp., but rapidly when heated; the product is better with ammonium than with potassium polysulphide. L. J. Gautier-Bouchard used ammonium polysulphide. J. W. Döbereiner, and M. Firmenich used potassium polysulphide. A. Ditte attributed the action of alkali sulphides to the alternate formation and decomposition of double alkali mercuric sulphide; he said that $K_2S.5HgS$ is formed and decomposed at 45° with the deposition of the red crystalline sulphide, whilst the liberated alkali sulphide forms more double salt, and so the cycle continues anew. M. C. Mehu said that mercuric sulphide is insoluble in either sodium hydroxide or sulphide, but it is soluble in a mixture of the two; when the soln. is diluted, the black sulphide is deposited, but when carbon dioxide is passed through the soln., cinnabar is formed. L. L. de Koninck found that mercuric sulphide is very soluble in conc. soln. of the alkali and alkaline earth sulphides, but not in soln. of the hydrosulphides. When the soln. are rapidly diluted, black amorphous sulphide is precipitated, but when slowly diluted, red cinnabar is obtained. S. B. Christy, and J. A. Ippen heated amorphous mercuric sulphide in a sealed tube with alkaline soln. sat. with hydrogen sulphide and obtained cinnabar at 200°–250°; S. B. Christy said the reaction is retarded by the presence of carbon dioxide. C. Brunner compared the action of potassium, sodium, and ammonium polysulphides. G. S. C. Kirchhoff, and C. F. Bucholz employed a soln. of potassium hydroxide with sulphur in place of the polysulphide. A. Eibner used soln. of polysulphides of potassium, calcium, or

barium sat. with sulphur, and various compounds of mercury. V. Stanek obtained red mercuric sulphide by heating the precipitated sulphide with white ammonium sulphide in a sealed tube at 150°–200°. It is difficult to remove all the alkali sulphide and sulphur from vermilion prepared by the alkali sulphide process, and these impurities are detrimental to the product. H. W. Picton and S. E. Linder recommended suspending the black sulphide in water, and passing in a stream of hydrogen sulphide until all is dissolved. Vermilion is precipitated when the soln. is heated in closed vessels to 160°–170° for several hours. C. Brunner employed mercuric oxide, mercurous chloride, and basic mercuric sulphate; J. von Liebig, infusible white precipitate; U. Alvisi used mercuric ethyl sulphide, mercuric ethyl chlorosulphide, mercurous chloride, etc., with ammonium sulphide, or hydrogen sulphide with an acidic or alcoholic soln. of mercuric ethyl sulphide. E. Weinschenk prepared cinnabar by heating a soln. of mercuric chloride and ammonium thiocyanate in a sealed tube between 230° and 250° for 4–6 days. Both red and black sulphides were formed; the ammonium thiocyanate served to generate hydrogen sulphide. W. J. S. Grawitz dissolved mercuric oxide in a soln. of sodium thiosulphate, and precipitated the red sulphide by adding ammonium chloride, and warming the soln.; O. Hausamann heated a soln. of infusible white precipitate in a conc. soln. of sodium thiosulphate; F. J. Faktor similarly treated a soln. of mercuric chloride, F. Field a soln. of mercuric iodide, and H. Fleck a soln. of potassium mercuric thiocyanate, or sodium mercuric chloride in the same solvent. The reaction has also been studied by E. T. Allen and J. L. Crenshaw—*vide supra*. J. Schröder passed hydrogen sulphide into a soln. of mercuric bromide or iodide in pyridine, and obtained a red sulphide; with soln. of the chloride the precipitate was at first black and then red; and with very dil. soln. the thiochloride was formed. F. Bezold obtained the red sulphide by the action of an ammoniacal soln. of hydrogen sulphide on a soln. of mercuric iodide in methyl acetate—M. Hamers used ethyl acetate. E. Gerlach electrolyzed a soln. of 8 grms. ammonium citrate, 8 grms. of sodium nitrate, and 100 grms. of water in the presence of sulphuric acid. The deep red modification of mercuric sulphide, designated β-HgS, which is not cinnabar, was prepared by E. T. Allen and J. L. Crenshaw from soln. containing 10 per cent. of mercuric chloride and sodium thiosulphate with 2 per cent. of sodium chloride, provided the ratio $HgCl_2 : Na_2S_2O_3$ was between 1 : 1 and 1 : 4.

According to E. T. Allen and J. L. Crenshaw, when the red powder formed by the action of ammonium sulphide is sublimed in an evacuated glass tube, the sublimate is quite black. If the layer on the walls of the tube is very thin, or cooled with sufficient rapidity, it is entirely black, but in thick layers, the product is practically all coarsely crystallized cinnabar coated with a thin layer of black sulphide. It is not possible to say definitely if this coating is amorphous or if it is metacinnabarite. R. Kempf sublimed mercuric sulphide under 12 mm. press. at 400° and obtained metacinnabarite; W. Spring obtained it by subliming ordinary mercuric sulphide in an atm. of an indifferent gas—carbon dioxide, or nitrogen; H. Arctowsky, by heating a mixture of sulphur and mercuric chloride in an atm. of hydrogen; and E. T. Allen and J. L. Crenshaw, by boiling 6 grms. of mercuric chloride, 60 grms. of sodium chloride, and 12 grms. of sodium thiosulphate in 4 litres of water and 10 c.c. of 30 per cent. sulphuric acid, washing the precipitate with alcohol and ether, then with carbon disulphide, and finally drying in vacuo at 250°. J. M. Séguin converted cinnabar into the black sulphide by heating it out of contact with air; if the temp. is too high, cinnabar sublimes, and if the black colour is to be retained on cooling, the cinnabar must be heated until it begins to volatilize, and immediately the sublimation of the sulphide began, J. N. von Fuchs plunged the tube of mercuric sulphide into cold water. The red sulphide blackens when heated to 320°, and the red colour is restored by fast or slow cooling; if heated to 410°, W. Spring found that the black colour remains on cooling; and he converted some red into black sulphide by trituration. M. Roloff converted red into black sulphide by exposure to light, and K. Heumann said that the transformation

is dependent on the presence of moisture ; it does not occur when the red sulphide is under acids, but under alkaline soln. it proceeds faster than under water.

Black amorphous sulphide is produced with the development of heat when the two elements are triturated at ordinary temp. If other than eq. proportions are used, the excess of either element remains in a free state, and C. G. Mitscherlich removed the excess of sulphur with carbon disulphide, and M. af Rosenschöld, the excess of mercury with dil. nitric acid. T. W. C. Martius agitated the mixture by fixing the containing bottle to the beam of a sawmill. F. D. Lichtenberg warmed the mortar in which the trituration was made ; if heated too strongly, some red sulphide was formed. A. Monheim triturated equal parts of sugar, sulphur, and mercury with a little water and afterwards washed out the sugar ; P. L. Geiger likewise triturated a mixture of sulphur and mercury with about 10 per cent. of ammonium sulphide, and P. R. Destouches used potassium sulphide. The soluble sulphides were afterwards removed by washing. R. von Schrötter found that when a piece of sulphur is placed in a barometric vacuum, in darkness, the black sulphide is formed in a few days ; in light, some red sulphide is also formed. J. Dewar noted the formation of the black sulphide at the temp. of liquid air. When mercury is agitated with an excess of an aq. soln. of ammonium or alkali polysulphide, the black sulphide is formed, and if sulphur is added, the polysulphide is reformed, and the conversion of the mercury is completed.

According to C. Barfoed, mercurous salts with hydrogen sulphide, or colourless ammonium sulphide, give a mixture of black amorphous sulphide and mercury. L. Freundt made the black sulphide by digesting a soln. of mercurous nitrate with washed flowers of sulphur, but G. Vortmann and C. Padberg found that but little sulphide is formed when mercurous sulphide is boiled with sulphur and water. A. Baumé found black mercuric sulphide is precipitated by hydrogen sulphide or alkali hydrosulphides from soln. of mercuric salts—E. Weinschenk stated that the precipitate is the cinnabar not the metacinnabarite modification. Alkali chlorides were found by E. Rupp to favour the coagulation of the precipitate. U. Antony and Q. Sestini mixed soln. of hydrogen sulphide and an aq. suspension of mercurous chloride or acetate. N. Tarugi mixed soln. of mercuric thioacetate and ammonium sulphide. J. H. Thwaites found zinc sulphide precipitated mercuric sulphide from cold soln. of mercuric salts. J. Schröder found dry pyridine soln. of mercuric chloride or cyanide gave the black sulphide when treated with dry hydrogen sulphide, and the red sulphide with analogous soln. of mercuric bromide or iodide. F. J. Faktor obtained the black sulphide by the action of dry sodium thiosulphate on mercuric chloride ; when cinnabar is sublimed from sodium thiosulphate, the black sulphide is formed, and the product is reddened by trituration.

According to F. Cornu,[5] native black amorphous mercuric sulphide is colloidal. A. Lottermoser prepared **colloidal mercuric sulphide** by the action of hydrogen sulphide on a finely divided suspension of mercuric oxide ; he also dialyzed the deep soln. obtained by passing hydrogen sulphide into a soln. of mercuric cyanide. H. R. Procter and R. A. S. Jones precipitated mercuric sulphide from a soln. of mercuric salts in the presence of certain organic acids—formic or citric acid. C. Winssinger, and H. W. Picton and S. E. Linder suspended in water the precipitate produced by passing hydrogen sulphide into a soln. of mercuric chloride, and passed hydrogen sulphide in excess through the liquid. It was suggested by H. W. Picton and S. E. Linder that the products are *mercuric hydrosulphides*, $HgS.nH_2S$. J. Lefort and P. Thibault treated a soln. of gum arabic and mercuric chloride with sodium sulphide. J. Hausmann allowed a soln. of mercurous nitrate to diffuse into a 5 per cent. gelatine soln. of ammonium sulphide. W. Leuze treated a soln. of sodium protalbinate or lysalbinate with one of mercuric chloride. A. Pieroni added a soln. of hydrogen sulphide in pyridine to a soln. of mercuric acetate in the same solvent. E. W. Lewis and H. Waumsley treated mercury with carbon disulphide containing about 0·5 per cent. of caoutchouc, and 10 per cent. of benzene.

The physical properties of mercuric sulphide.—According to E. T. Allen and J. L. Crenshaw,[6] the **colour** of the mercuric sulphide powder formed by ammonium sulphide is a lighter scarlet-red than that prepared by using an excess of alkali sulphide. The difference is solely one of subdivision, the darker product consists of crystals easily recognized by the naked eye, and the colour of these, when ground in a mortar, is scarcely distinguishable from that of the powder made by using ammonium sulphide. The colour of cinnabar varies from scarlet-red to brownish-red and lead-grey. B. F. Hill has described ruby-red crystals of cinnabar, and P. W. Jeremejeff, a variety cochineal red about the edges, and lead-grey in the thicker parts. When heated, vermilion-red acquires a brownish tinge, and it becomes quite brown at 250°, and black at a higher temp. If the temp. has not been up to the point of volatilization—400°, according to E. T. Allen and J. L. Crenshaw—the scarlet colour is restored on cooling; otherwise the colour remains black, as previously indicated. The temp. at which cinnabar becomes permanently black is not an inversion point. E. T. Allen and J. L. Crenshaw's hexagonal form, β-HgS, has rather a deeper red colour than ordinary cinnabar, but it is not distinguishable from cinnabar by colour alone. Metacinnabarite is black, with a reddish or brownish streak. The amorphous sulphide is black. The colloidal soln. are black, or if dil., brown.

Metacinnabarite forms hexacistetrahedral **crystals** belonging to the cubic system. They were studied by A. Schrauf,[7] W. H. Melville, M. François and C. Lormand, H. Arctowsky, G. E. Moore, W. Spring, E. T. Allen and J. L. Crenshaw, etc. The crystals of the artificial black sulphide, α'-HgS, have not been definitely identified with the native mineral on account of the minute size and poor development. The crystals show typically six spindle-shaped rays apparently equal, and meeting at right angles—so that they indicate a skeletal growth parallel to the axes of the cube. J. B. L. Romé de l'Isle supposed the crystal form of cinnabar to be probably tetrahedral, and R. J. Haüy showed them to be hexagonal. In a *Monographie der Krystallformen des Zinnobers*, A. Schabus reported the axial ratio to be $a:c=1:1{\cdot}1453$, and $\alpha=92°\ 30'$. Artificial cinnabar forms red hexagonal prisms or plates. Different forms were investigated by A. des Cloizeaux, O. Mügge, A. Schmidt, H. Traube, E. T. Allen and J. L. Crenshaw, etc. E. T. Allen and J. L. Crenshaw's modification, β-HgS, is prismatic in habit, and has been obtained in crystals not exceeding 0·003 mm. in width, and 0·03 mm. in length; the crystals taper towards the ends, and have no distinct faces. They are generally aggregated in stellate groups. F. Haber found by **X-radiograms** that the amorphous precipitate of mercuric sulphide has a great tendency to assume the crystalline state. C. Mauguin was unable to establish the character of the space-lattice from his observations on the X-radiograms of cinnabar.

According to R. Boyle, the **specific gravity** of different samples of cinnabar ranges from 7·57 to 8·1. C. J. B. Karsten gave 8·0602 for the sp. gr. of sublimed cinnabar; P. F. G. Boullay gave 8·124; E. T. Allen and J. L. Crenshaw gave 8·176 for the sp. gr. of purified red mercuric sulphide at 25°/4°; and W. Spring gave for the sp. gr. and **specific volume** of precipitated red mercuric sulphide:

	21·6°	23·5°	34·4°	34·6°	56·6°	77·7°
Sp. gr. . .	8·1289	8·1246	8·1004	8·1016	8·0830	8·0886
Sp. vol. . .	123·018	123·082	123·450	123·432	123·675	123·629

and of sublimed red mercuric sulphide:

	15·8°	18·0°	34·6°	56·7°	77·5°	77·7°
Sp. gr. . .	8·1587	8·1464	8·1181	8·0906	8·0979	8·0978
Sp. vol. . .	122·569	122·754	123·182	123·588	123·488	123·490

E. T. Allen and J. L. Crenshaw gave 7·20 for the sp. gr. of β-HgS at 25°/4°. G. E. Moore gave 7·701–7·748 for the sp. gr. of metacinnabarite; W. H. Melville, 7·095–7·142; A. Schrauf, 7·766; S. L. Penfield, 7·81; and E T. Allen and

J. L. Crenshaw, 7·60, at 25°/4°. W. Spring gave 124·385 for the sp. vol. of metacinnabarite. W. Ortloff computed the **molecular volume** of cinnabar to be 28·75; and metacinnabarite, 29·99. G. E. Moore gave 7·552 for the sp. gr. of amorphous black mercuric sulphide; and W. Spring, 7·5543 at 20°. The latter also gave for the sp. gr. and sp. vol. of the amorphous sulphide:

	18·3°	23·6°	35·4°	56·5°	56·6°	77·5°	77·8°
Sp. gr. . .	7·6242	7·6047	7·5697	7·5500	7·5494	7·5578	7·5610
Sp. vol. . .	131·160	131·496	132·106	132·452	132·454	132·313	132·225

The **hardness** of native cinnabar is 2 to 3·5 on Mohs' scale; and G. E. Moore gave 3·3 for that of metacinnabarite. A. Ries and L. Zimmermann have discussed this subject.

The **coefficient of thermal expansion** of cinnabar, according to H. Fizeau,[8] is $\alpha=0{\cdot}00002147$ parallel to the principal axis, and 0·00001791 perpendicular to that axis when the temp. is 40°; the temp. coeff. of the former is $d\alpha/d\theta=0{\cdot}0_7151$, and of the latter, $0{\cdot}0_7063$. According to E. Jannetaz, the sq. root of the ratio of **thermal conductivity** of cinnabar in the direction of the principal axis to that in the direction of the base is 0·85; L. Godard also measured the diffusion of heat in cinnabar. H. Kopp gave 0·0517 for the **specific heat** of cinnabar between 12° and 51°; H. V. Regnault, 0·0512 between 14° and 98°; F. Streintz, 0·0548; A. A. de la Rive and A. Marcet gave 0·0597; A. Sella, 0·0529; and W. Spring gave:

	25°–30°	35°–40°	45°–50°	55°–60°	65°–70°	75°–80°
Sp. ht. . .	0·0749	0·0871	0·0934	0·0985	0·1074	0·1270

A. S. Russell gave 0·0391 between −189° and −79°; 0·0488 from −74° to 0°; and 0·0515 from 2° to 49°. H. V. Regnault gave 0·0512 for the sp. ht. of the black sulphide between 14° and 98°; F. Streintz gave 0·1026; and W. Spring:

	25°–30°	35°–40°	45°–50°	55°–60°	65°–70°	75°–80°
Sp. ht. . .	0·0835	0·0967	0·1102	0·1103	0·1206	0·1433

M. Goldstein gave 5·9 for the **molecular heat** of cinnabar. E. Tiede and A. Schleede found that although mercuric sulphide sublimes without melting when heated under atm. press., the **melting point** is 1450° under a press. of 120 atm., furnishing a steel-grey matt solid which becomes red when rubbed. Mercuric sulphide volatilizes without melting at atm. press. According to E. T. Allen and J. L. Crenshaw, the **vapour pressure** reaches one atm. at 580°. and the compound is stable over the whole temp. range up to the volatilization point. The other two forms are monotropic, because at 100°, both α'-HgS and β-HgS are changed into cinnabar with a soln. of ammonium sulphide, while at 200°, the same change occurs slowly in sealed tubes with 30 per cent. sulphuric acid; and at 400°, 450°, 500°, and 550°, both are transformed into cinnabar when heated alone in evacuated glass tubes. C. Zenghelis stated that cinnabar volatilizes slightly at ordinary temp. in vacuo. G. F. Hildebrandt stated that it sublimes in closed vessels without decomposition and without residue. According to F. Damm and F. Krafft, volatilization begins at 400° when cinnabar is exposed to the cathode light in vacuo. W. Biltz gave the volatilization temp. of cinnabar as 446°±10°, and A. de Gramont found that it volatilizes rapidly in the electric arc. A. Schrauf stated that metacinnabarite begins to volatilize in air at 240°. E. Mitscherlich found the **vapour density** to be between 5·51 and 5·99; V. and C. Meyer gave 5·39—calculated for a mixture of Hg and S_2, 5·34. A. Schrauf estimated the minimum mol. wt. to be Hg_3S_3; and A. Scott calculated the mol. wt. to be 151·8 at high temp.

J. Thomsen[9] found the **heat of formation** to be (Hg, S)=16·89 Cals.; and $Hg(NO_3)_2aq.+H_2Saq.=HgS+2HNO_3+38{\cdot}87$ Cals.; and M. Berthelot gave for $(Hg, S)_{\text{black precipitate}}$ 10·6 Cals. The black amorphous sulphide, according to R. Varet, is transformed into the red amorphous sulphide with the evolution of 0·24 Cal.,

and into the red crystalline form with 0·30 Cal.; so that the transformation of red amorphous into red crystalline is attended by the evolution of 0·06 Cal.

A. des Cloizeaux [10] found the **refractive index** of cinnabar for red light to be $\omega=2{\cdot}854$, and $\epsilon=3{\cdot}201$; and for the Li-ray, $\omega=2{\cdot}816$, and $\epsilon=3{\cdot}142$. K. Zimanyi also measured the refractive index of Almaden cinnabar. H. E. Merwin and co-workers found $\omega=2{\cdot}81$, and $\epsilon=3{\cdot}14$ for the Li-ray; for the hexagonal β'-HgS, $\omega=2{\cdot}58$, and $\epsilon=2{\cdot}85$, for a ray $\lambda=650\mu\mu$ and the dispersion $\epsilon-\omega=0{\cdot}24$. The crystals of mercuric sulphide have a high refractive index. Cinnabar and meta-cinnabarite have a strong positive double refraction, and they are optically uniaxial. The **circular polarization** of cinnabar was studied by A. des Cloizeaux, G. Wyrouboff, G. Tschermak, and W. H. Melville and W. Lindgren. The **dispersion** of cinnabar crystals was measured by H. Rose, and found to deviate from Drude's and Ketteler's formulæ. E. L. Nichols and B. W. Snow measured the **reflecting power** of cinnabar for rays of different wave-length between 25° and 220°. A. de Gramont found that the **spark spectrum** of cinnabar showed the lines 579, 577, 546, 436, and $404\mu\mu$, as well as many sulphur lines. K. Heumann found that cinnabar exhibits **thermo-luminescence** glowing with a feeble white glow—J. Calafat y Leon said a blue glow—when heated. S. M. Losanitsch found specimens of cinnabar from Alva and Bare (Serbia) and Idria (Austria) have a smaller **radioactivity** than pitchblende. Other mercury minerals examined were inactive. The barytes which accompanies the active cinnabar is inactive, from which it is concluded that radium is absent and that the activity is due to a "radio-mercury." The activity is completely removed by igniting the mineral. According to A. Verneuil, the presence of $\frac{1}{1000}$th part of mercuric sulphide in calcium sulphide changes the colour but not the intensity of the phosphorescence. B. Gudden and R. Pohl, and H. Rose found cinnabar showed a **photoelectric effect**; and H. Rose studied the effect of temp. on the refraction of light by cinnabar, and also the absorption spectrum of that compound. The coagulation of colloidal mercury sulphide in light was observed by P. B. Ganguly and N. R. Dhar.

A. de Gramont,[11] and G. Cesaro found that cinnabar has a feeble **electrical conductivity.** The conductivity was found by J. Gibson to increase on exposure to light. R. G. van Name said the conductivity of red and black mercuric sulphides amounts to $0{\cdot}01$ to $0{\cdot}02\times10^{-6}$. According to G. Karsten, F. Beyerinck, and G. Cesaro, metacinnabarite is a good conductor. Black mercuric sulphide was found by F. Streintz to conduct well when pressed into rods under a press. of 10,000–13,000 atm. The resistance falls from 41 ohms at 16° to 11·1 ohms at 100° and rises to about 25 ohms at 140°. W. Mönch made observations on this subject. C. H. Hall found colloidal mercuric sulphide suspended in oil is not precipitated by alternating or direct currents of voltages 10^4 to 2×10^5.

The chemical properties of mercuric sulphide.—Black mercuric sulphide reacts chemically much the same as the red sulphide, only more vigorously. K. Heumann [12] found that red mercuric sulphide prepared by digestion with ammonium sulphide is decomposed more rapidly by exposure to *light* than is the case with that prepared by sublimation. In water-colour painting, said A. H. Church, most vermilions are found to be changed on exposure, the solar rays gradually converting the red into the black sulphide without producing any chemical alteration. This change occurs even in the absence of air and moisture. Impure air, *per se*, even if hydrogen sulphide be present, does not alter vermilion. W. D. Bancroft added that the varnish on a picture cuts off the ultra-violet light to a very great extent, and protects the picture in this way, in addition to keeping out moisture and gases. Red mercuric sulphide was found by K. Heumann to be blackened when exposed to sunlight under conc. aq. ammonia, but there is no separation of sulphur or mercury. Commercial sublimed vermilion is superficially blackened in a few minutes when kept under conc. aq. soln. of ammonia, or alkali hydroxide, and with vermilion prepared in the wet way, the blackening occurs in a couple of seconds. When preserved for a long time under water acidified with nitric

acid, vermilion showed no signs of blackening ; if the vermilion prepared in the wet way contains traces of mercurous nitrate, it is blackened in darkness when confined under a soln. of ammonia or sodium hydroxide ; boiling the product with dil. nitric acid restores the red colour. W. Ramsay and M. W. Travers found that native cinnabar contains occluded carbon monoxide.

H. Pélabon found that **hydrogen** reacts slowly with crystalline cinnabar at 280° ; and in a closed vessel, equilibrium is attained in about 90 hrs. at 360° when about 78·67 per cent. of hydrogen sulphide is present ; at 440°, there is 85·29 per cent. ; and at 540°, 92·10 per cent. The ratio $H_2 : H_2S$ is dependent on the initial press., and is smaller in the presence of an excess of mercury. G. Pollacci found that the moist precipitated sulphide is oxidized more quickly than cupric sulphide. According to G. F. Hildebrandt, when cinnabar is heated in air, it burns with a blue flame, forming sulphur dioxide and the metal. K. Friedrich stated that no decrepitation occurs when cinnabar is heated in air or **oxygen ;** sulphur dioxide begins to be formed between 230° and 297°—depending on the grain-size ; fumes begin to appear between 348° and 430° ; and the mass ignites between 380° and 450°. F. Janda has studied the changes which occur during the roasting of cinnabar for the metal—*q.v.* A. Mailfert found **ozone** reacts slowly with mercuric sulphide, converting it into sulphate. H. V. Regnault observed that at a red heat **water** vapour furnishes hydrogen sulphide, a black sublimate, much metallic mercury, but no mercury oxide. G. A. Binder found that distilled water acting on cinnabar for 5 weeks at 90° dissolves traces of the mineral. According to G. Bodländer, mercuric sulphide is less soluble in water than is silver or cuprous sulphide. O. Weigel found that a litre of water dissolved $0{\cdot}054\times10^{-6}$ mol of precipitated mercuric sulphide ; and J. Knox that a litre of water at 24° dissolves $1{\cdot}7\times10^{-27}$ mol, and the solute is completely dissociated. P. de Clermont and M. Frommel found that the precipitated sulphide is not decomposed by water at 100°. T. M. Broderick found that cinnabar is dissolved by natural chloride-waters but not by sulphide-waters. W. Spring believed that **mercuric oxytrisulphide,** $HgO.3HgS$, is formed by boiling the sulphato-sulphide, $HgS.3HgSO_4$, with water ; but T. Poleck doubted the existence of the oxysulphide. In all reactions examined by T. Poleck and C. Goercki a mixture of the sulphide and oxide was formed, and the latter was removable by dil. hydrochloric, sulphuric, or acetic acid, by formamide, or by digestion with a soln. of potassium iodide at 140°.

According to F. Field,[13] cinnabar burns in **chlorine** with incandescence, forming sulphur chloride, S_2Cl_2, and mercuric chloride ; when boiled with a mixture which develops chlorine—say, manganese dioxide or antimonic or arsenic oxide and hydrochloric acid—mercuric chloride and sulphur are formed ; and when treated with **aqua regia,** it dissolves quantitatively as mercuric chloride—only a little sulphuric acid is formed. G. F. Hildebrandt, and J. B. Hannay also noted the solubility of cinnabar in aqua regia ; A. Schrauf also found that metacinnabarite dissolves in cold aqua regia with the separation of flocculent sulphur. E. Schäfer found cinnabar to be slowly decomposed by **bromine** at ordinary temp. and rapidly when heated, while E. Filhol and J. Melliès stated that **iodine** alone or in ethereal, chloroform, or aq. soln. acts on mercuric sulphide alone, or suspended in water or alcohol, forming mercuric iodide ; and R. Wagner found that a soln. of iodine in potassium iodide decomposes cinnabar : $HgS+2KI+I_2=S+K_2HgI_4$. B. S. Neuhausen studied the action of iodine on mercuric sulphide. According to M. Berthelot, hydrogen chloride decomposes cinnabar. G. F. Hildebrandt said that **hydrochloric acid** has no action. U. Antony and L. Niccoli also found that hot acid of medium conc. has no action on mercuric sulphide ; but, according to S. M. Jörgensen, the conc. boiling acid gives a little hydrogen sulphide, and, when the soln. cools, yellow mercuric thiochloride is deposited. M. Berthelot said that mercuric sulphide is decomposed by fuming hydrochloric acid. According to W. B. Rising and V. Lehner, mercuric sulphide readily dissolves in boiling 20 per cent. **hydrobromic acid** furinshing hydrogen sulphide and mercuric bromide ; and,

according to S. M. Jörgensen, the conc. acid attacks mercuric sulphide in the cold, and when warmed a colourless soln. is quickly formed. A. Kekulé stated that conc. **hydriodic acid** dissolves mercuric sulphide in the cold; but the dil. acid required to be heated.

Salts of the hypothetical acid $H_2S.HgS$, or H_2HgS_2, are known. H. W. Picton and S. E. Linder [14] found that when **hydrogen sulphide** is passed into water containing mercuric sulphide in suspension, some of the latter is dissolved—10 grms. per litre—this is probably colloidal, since, according to J. Knox, the conc. of the complex which is formed is of the order 10^{-14} mol per litre. J. N. Mukherjee and N. N. Sen found that a soln. of hydrogen sulphide stabilizes mercuric sulphide sol against coagulation and an increased stability occurs with ammonium and potassium chlorides, and a decrease with barium and strontium chlorides. The stability of the sol is also increased by dilution irrespective of the nature of the electrolyte. The data which have been published on the solubility of mercuric sulphide in soln. of **alkali sulphides** and **alkali hydrosulphides** are contradictory. M. C. Mehu stated that mercuric sulphide is insoluble in either sodium hydroxide or sodium sulphide, but that it is soluble in a mixture of the two; however, according to L. L. de Koninck, mercuric sulphide is very soluble in conc. soln. of the alkali sulphides—even in the absence of alkali hydroxides—and in those of the alkaline earths, but is not soluble in soln. of the hydrosulphides or in ammonium sulphide, $(NH_4)_2S$. G. F. Becker found that this statement is true only for cold soln., for when heated with a soln. of sodium hydrosulphide, mercuric sulphide dissolves; it is also soluble in soln. of sodium sulphide and in mixtures of the two. Mercuric sulphide is completely soluble in a mixed soln. of sodium hydroxide and sulphide when the ratio HgS : Na_2S is 1 : 2. According to R. Weber the solubility is conditioned by the formation of double salts which were afterwards studied by A. Ditte. The presence of sodium carbonate does not retard the dissolution of mercuric sulphide in sodium sulphide soln., but within certain limits a part of the mercury is precipitated if borax be present. A. Schrauf found that metacinnabarite is completely soluble in colourless potassium hydrosulphide; and all three crystalline modifications were found by E. T. Allen and J. L. Crenshaw to be soluble in soln. of potassium and sodium monosulphides. V. Stanek found white ammonium sulphide transforms the red into black sulphide at 150°–200° in a sealed tube. According to L. L. de Koninck, the addition of a large proportion of water to a soln. of alkali mercuric sulphide precipitates mercuric sulphide, but not if alkali hydroxide be also present. Ammonium chloride, according to K. Polstorff and K. Bülow, also precipitates mercuric sulphide from its soln. in alkali sulphides. M. Berthelot found that the precipitation begins when acetic acid is added to the soln. of alkali mercuric sulphide even if the soln. is alkaline, and it is complete in an acid soln. L. L. de Koninck also added that if the precipitation be rapid, the black sulphide appears; if slow, the red sulphide. E. Behrend estimated that a soln. of mercuric sulphide in sodium sulphide has a mgrm. of Hg-ions per 2×10^{17} litres for the conc. of the S''-ions or the $Hg^{\cdot\cdot}$-ions; J. Knox gave $1{\cdot}7\times10^{-27}$ gram-ions per litre, and L. Bruner, and J. Zawadzky gave $9{\cdot}0\times10^{-31}$. J. Knox studied the solubility of mercuric sulphide in soln. of the alkali sulphides and in soln. of barium sulphide. He found the solubility in potassium sulphide soln. to be greater than in sodium sulphide soln. Expressing the results in mols per litre, J. Knox found with potassium sulphide:

Conc. of K_2S	1·0	0·5	0·25
Solubility HgS, red	0·4629	0·1588	0·04839
Solubility HgS, black	—	0·1836	0·06000

and with sodium sulphide:

Conc. of Na_2S	2·030	1·52	1·015	0·755	0·50	0·25	0·10
Solubility HgS, red	1·144	0·7832	0·4423	0·2878	0·1500	0·04544	0·00824
Solubility HgS, black	—	0·8561	0·5002	0·3336	0·1805	0·05622	0·01085

In the case of sodium sulphide soln. the anions HgS_2'' are formed, and this the more

with increasing dilution, and with the black sulphide more readily than with the red. The solubility decreases with rise of temp., so that the temp. coeff. between 25° and 33° is small and negative.

Conc. of Na_2S	0·755	0·50	0·25	0·10
Solubility at 33°	0·2828	0·1465	0·04360	0·007887
Solubility at 25°	0·2878	0·1500	0·04544	0·00824

The solubility is augmented if sodium hydroxide be present.

Conc. of Na_2S	1·015	0·755	0·50	0·25	0·10
Solubility HgS	0·4423	0·2878	0·1500	0·04544	0·008241
with 0·5*N*-NaOH	—	—	0·2843	0·1106	0·03962
1·0*N*-NaOH	0·673	0·485	0·302	0·148	0·0563
4·67*N*-NaOH	—	—	—	0·225	0·0903
7·7*N*-NaOH	0·9167	—	0·4637	0·2369	0·09634

In soln. sat. with sodium sulphide, J. Knox found $[Hg^{\cdot\cdot}][HgS_2'']=4\times10^{-53}$; and for the complex anion, $5{\cdot}1\times10^{-54}[Hg^{\cdot\cdot}][S'']^2=[HgS_2'']$. J. Knox calculated the equilibrium constant from the data of C. Immerwahr to be $7{\cdot}0\times10^{-26}$; and obtained for the solubility product $[Hg^{\cdot\cdot}][S'']=2{\cdot}8\times10^{-54}$ at 25°. R. Abegg stated that the solubility of cinnabar in alkali sulphide soln. is proportional to the conc. of the S″-ions. The solubility of mercuric sulphide in soln. of sodium disulphide, Na_2S_2, is about half as great as in the corresponding soln. of sodium monosulphide, Na_2S. The solubility with barium sulphide soln. is virtually the same as with sodium sulphide soln.—being 0·008241 mol. HgS per litre with a soln. containing 0·1 mol. BaS.

E. F. Smith found that **sulphur monochloride,** S_2Cl_2, dissolves cinnabar. According to H. Feigel, a benzene soln. of sulphur chloride converts mercuric sulphide into a yellow compound, *mercuric sulphochloride*, HgS_2Cl_2; mercuric sulphide is also coloured yellow when allowed to stand in contact with sulphur chloride. A. Guerout found that it is not changed by aq. **sulphurous acid.** According to G. F. Hildebrandt, and W. T. Brande, cold conc. **sulphuric acid** does not act on red or black mercuric sulphide, but the hot acid develops sulphur dioxide with the sublimation of sulphur and the formation of mercuric sulphate—M. Berthelot did not detect the formation of hydrogen sulphide at any temp. E. Divers and T. Shimidz uobtained white sulphatosulphide, $2HgS.HgSO_4$, with hot conc. sulphuric acid; and A. Schrauf obtained white mercuric sulphate by the action of boiling sulphuric acid on metacinnabarite. W. C. Moore detected no perceptible action with a mixture of 4*N*-HNO_3 and 4*N*-H_2SO_4 after 100 days at ordinary temp.; there is a slight action in 14 days at 25·75°; when boiled under a reflux condenser, the oxidation of the mercuric sulphide is rapid.

According to G. Gore,[15] mercuric sulphide is insoluble in liquid **ammonia**, and G. F. Becker found it to be soluble in aq. ammonia when heated in a sealed tube at 145°–175°, but K. Heumann observed no action at ordinary temp. and press. H. Moissan found mercury reacts with **sulphammonium** at ordinary temp., forming a crystalline *mercury sulphammonium* which dissociates into black mercuric sulphide. G. F. Hildebrandt, and U. Antony and L. Niccoli said that cinnabar is not affected by long boiling with **nitric acid;** C. Barfoed observed no action when heated 48 hrs. with nitric acid of sp. gr. 1·52 at 70°–72°, and the precipitated sulphide is not attacked by conc. nitric acid of sp. gr. 1·52 after many hours' contact in the cold, but after 24 hrs. at 70°–75°, the sulphide becomes grey, and after standing another 24 hrs., sulphuric acid is formed, a trace of mercury is dissolved, and the solid residue is mercuric nitratosulphide, $2HgS.Hg(NO_3)_2$. J. Torrey also stated that the precipitated black sulphide is changed by boiling dil. nitric acid into brown, yellow, or white nitratosulphide, which is again blackened by a boiling soln. of sodium carbonate. F. Gramp found that with nitric acid of sp. gr. 1·4 in a sealed tube at 120°, mercuric sulphide is rapidly and completely oxidized to mercuric sulphate; with an acid of sp. gr. 1·2, the residue has the composition HgO, 6HgS, $2Hg(NO_3)_2$,

$12H_2O$. J. L. Howe found that mercuric sulphide is not changed by boiling with pure nitric acid (sp. gr. 1·42); the addition of one drop of dil. hydrochloric acid, however, causes the conversion of the sulphide into a yellowish-white compound, presumably $Hg(NO_3)_2$, $2HgS$; the further addition of 10 drops of hydrochloric acid causes the complete soln. of the yellowish compound. The same changes are brought about by dil. nitric acid containing a little hydrochloric acid as impurity. Similar observations were made by W. C. Moore with a mixture of nitric acid and potassium chloride—the mercuric sulphide is more or less vigorously oxidized—*vide supra* for the action of aqua regia. R. F. Weinland and L. Storz found no reduction occurred when mercuric sulphide is boiled with a soln. of **sodium arsenite,** Na_2AsO_3. L. Storch found that cinnabar is dissolved by soln. of sodium or ammonium **thioarsenate, thioantimonate, thiostannate, thiomolybdate, thiotungstate,** and **thiovanadate.**

According to F. C. Vogel,[16] when a mixture of mercuric sulphide and **carbon**—lampblack, or charcoal—is heated, decomposition occurs, mercury vapour is given off, and a large quantity of hydrogen sulphide is evolved—P. Berthier said that F. C. Vogel mistook carbon disulphide for hydrogen sulphide, and added that the decomposition is very incomplete. M. Berthelot found that freshly precipitated and well-washed mercuric sulphide does not dissolve in a soln. of **potassium cyanide,** nor does a soln. of potassium mercuric cyanide, K_2HgCy_4, give a precipitate with hydrogen sulphide. T. Rosenbladt found mercuric sulphide to be soluble in a soln. of **potassium thiocarbonate,** and to be reprecipitated by carbon dioxide. H. C. Bolton found that cinnabar resists the action of **citric acid,** J. Schröder found cinnabar to be insoluble in **pyridine.** According to G. Rauter, cinnabar is not decomposed by **silicon tetrachloride.**

According to G. F. Hildebrandt,[17] cinnabar is desulphurized when heated with **iron, copper, tin, lead, silver, bismuth,** or **antimony,** forming a sulphide, and mercury distils over. A. Eschka studied the action of iron. C. Karmarsch found that at ordinary temp. copper or **brass** is blackened by cinnabar only when impurities are present—*e.g.* potassium carbonate, but K. Heumann found that the vermilion loses its characteristic colour in contact with copper or brass; a slip (*i.e.* a suspension in water) of mercuric sulphide amalgamates copper; and metals generally desulphurize mercuric sulphide suspended in water—*e.g.* cinnabar suspended in water is immediately converted by **zinc** filings into a greyish-black powder; if the water is acidified the change is very rapid, and some hydrogen sulphide is formed. Powdered copper acts similarly on cinnabar suspended in water.

When cinnabar is ignited with an **alkali hydroxide** or **alkali carbonate,** P. Berthier [18] found that mercury is given off, and a mixture of the alkali sulphide and sulphate is formed. According to E. F. Smith, the sulphur of cinnabar is quantitatively oxidized if the powder is placed in molten potassium hydroxide and the containing nickel dish be made the anode for the electrolysis. J. Walker found mercuric sulphide to be soluble in a soln. of sodium hydroxide in the presence of the sulphides of the arsenic group; the mercury is precipitated by adding sodium peroxide to the boiling soln. Calcium oxide acts: $4CaO+4HgS=4Hg+3CaS+CaSO_4$. The decomposition is complete if the alkali or lime be mixed with some charcoal. P. Berthier also found that **lead oxide** under similar conditions furnishes sulphur dioxide and mercury, and leaves metallic lead and a fusible slag, which, if the lead oxide is not in great excess, contains undecomposed cinnabar.

According to A. Vogel, when cinnabar is heated with dry **stannous chloride,** mercuric chloride and a trace of sulphur dioxide are given off, and stannic sulphide is formed; and when cinnabar is boiled with an aq. soln. of stannous chloride, hydrogen sulphide and chloride are evolved and a brown mixture of undecomposed cinnabar and stannous chloride, mercury, and stannic oxide remains. When freshly precipitated mercuric sulphide is boiled with a soln. of **ferrous chloride,** J. B. Cammerer found only a trace of iron in the precipitate. F. Field found that soln. of **ferric chloride** or **cupric chloride** containing an excess of hydrochloric

acid are reduced when boiled for an hour with mercuric sulphide—sulphur separates at the same time; **chromic chloride** and **uranium chloride** are not affected. J. Hanus found a boiling soln. of ferric sulphate is not appreciably affected. E. Schürmann found mercuric sulphide at 100° is completely decomposed by a 0·1*N*-soln. of **palladious chloride,** but not by one of **silver nitrate** or **cupric sulphate.** According to P. A. Bolley, cinnabar is immediately blackened when immersed in a soln. of silver nitrate containing an excess of ammonia, and he recommends this as a test for cinnabar—silver sulphide, a basic mercuric nitrate, and a mercury amide are formed. Orpiment and stannic sulphide give the same reaction with silver nitrate soln., but without the ammonia.

The solubility of mercuric sulphide in soln. of various sodium sulphides has already been discussed. G. F. Becker [19] assumed that compounds $n\text{Na}_2\text{S.HgS}$ were formed, when n=1, 2, and 4, and possibly also 3 and $\frac{1}{2}$. J. Knox showed that aq. soln. contained the complex **sodium mercuric sulphide,** Na_2HgS_2; and he prepared the complex $2\text{Na}_2\text{S.5HgS.3H}_2\text{O}$, by concentrating a sat. soln. of mercuric sulphide in one of sodium sulphide, in vacuo over sulphuric acid, and removing the sodium sulphide by washing with oft-renewed absolute alcohol. The pale yellow crystals decompose in air, and they lose water in an atm. of hydrogen between 100°–105°, and are then coloured brownish-black.

A number of potassium mercuric sulphides has been prepared. According to C. Brunner, the liquid which is decanted from the cinnabar, prepared by G. S. C. Kirchhoff's process, is evaporated and decanted from the first crop of crystals; it is then further concentrated, and a mass of fine silky needles is obtained. These are dried by press. between filter paper; the analysis corresponds with **pentahydrated potassium mercuric sulphide,** $\text{K}_2\text{S.HgS.5H}_2\text{O}$. R. Weber made the crystals by dissolving freshly precipitated mercuric sulphide in a mixture of ammonium sulphide and potassium hydroxide. When the soln. is evaporated, ammonia is evolved and crystals of potassium chloride separate; when further conc., crystals of the pentahydrated sulphide appear, and they can be purified by re-crystallization from potassium hydroxide. R. Weber also mixed the freshly precipitated sulphide with a soln. of potassium hydroxide, and passed hydrogen sulphide through the soln. until all is dissolved—if too much hydrogen sulphide is introduced mercuric sulphide is precipitated because, said C. Barfoed, it has a low solubility in the hydrosulphide which is formed. The evaporation of the soln. furnishes the salt in question. R. Weber dissolved a mixture of equi-molar parts of sulphur and mercuric sulphide in an excess of molten potassium hydroxide, and evaporated the aq. soln. of the cold cake for crystals of the pentahydrate. According to R. Weber, the fine silky needles are deliquescent—probably because of the presence of free potassium hydroxide—they give off water when heated in a tube, and melt to a red liquid from which mercury, but not mercuric sulphide, sublimes. Water decomposes the salt with the separation of mercury and mercuric sulphide, according to C. Brunner, or of pentahydrated potassium pentamercuric sulphide, $\text{K}_2\text{S.5HgS.5H}_2\text{O}$, according to A. Ditte. A soln. of ammonium chloride acts like water (C. Brunner); neutral alkali hydroxide, sodium hydrophosphate, alkali hydrocarbonates, and borax soln. precipitate mercuric sulphide. A. Ditte prepared white silky needles of what he regarded, without analysis, as **heptahydrated potassium mercuric sulphide,** $\text{K}_2\text{S.HgS.7H}_2\text{O}$, from a soln. of freshly precipitated mercuric sulphide in a cold conc. soln. of potassium sulphide. A. Ditte also made **monohydrated potassium mercuric sulphide,** $\text{K}_2\text{S.HgS.H}_2\text{O}$, in golden-yellow plates by crystallization from a soln. of freshly precipitated mercuric sulphide in a hot conc. soln. of potassium sulphide.

By keeping pentahydrated potassium mercuric sulphide for a long time in contact with a soln. of potassium hydroxide in a closed vessel, R. Schneider obtained pale olive-green six-sided plates, probably rhombic, of **potassium dimercuric sulphide,** $\text{K}_2\text{S.2HgS}$. The crystals melt, forming a dirty brown mass, mercury and mercuric sulphide sublime, and a potassium polysulphide remains as a residue.

Water decomposed the double sulphide, depositing mercuric sulphide; chlorine forms sulphur chloride, S_2Cl_2, and mercuric and potassium chlorides; chlorine water oxidizes some of the sulphur to sulphuric acid; hydrochloric acid forms mercuric sulphide, hydrogen sulphide, etc.; aq. ammonia and potassium hydroxide separate mercuric sulphide; nitric acid acts like hydrochloric acid. A. Ditte also prepared black and red crystals of pentahydrated potassium pentamercuric sulphide, $K_2S.5HgS.5H_2O$. When mercuric sulphide is brought in contact with a dil. soln. of potassium sulphide, a certain quantity of the former is simply dissolved, but no other change takes place even if the substances are left in contact for several months. If, however, the alkaline soln. is moderately conc., the excess of mercuric sulphide is converted into brilliant black needles of the composition $K_2S.5HgS.5H_2O$, the change being more rapid the higher the temp. The crystals are larger and more brilliant the more slowly they are formed. They are decomposed by water, which gradually removes the alkaline sulphide and leaves a residue of mercuric sulphide, the decomposition taking place much more rapidly on heating. If the soln. of potassium sulphide is very highly conc. white needles of the heptahydrate are formed. Red needles of $K_2S.5HgS.5H_2O$, resembling the black needles in every respect except colour, are formed when a soln. of the alkaline sulphide containing an excess of mercuric sulphide is gradually heated to 35°–40°, especially if a small quantity of vermilion is added. In such a soln., heated at 35°–40°, but still clear, the formation of red or black needles is determined by adding a small quantity of vermilion or of the black crystals respectively. The colour of the crystals varies from bright red to deep cinnabar-red, according to the conc. of the soln. and the temp. When a mass of the black needles is allowed to stand in the alkaline sulphide soln. in a closed vessel for some time, those crystals which are in contact with the sides of the vessel are gradually converted into the red variety. These are stable in the alkaline liquid in the cold, but if heated they are converted into the black variety, the change being more rapid the more conc. the soln. If the alkaline sulphide soln. at the ordinary temp. contains but a small quantity of the compound HgS, K_2S, it yields on boiling a black deposit, which contains not only black crystals of $K_2S.5HgS.5H_2O$, but also mercuric sulphide in black hexagonal plates. If such a soln. is gradually heated in a water-bath and mixed with a trace of vermilion, a red deposit is obtained consisting of needles of the composition $K_2S.5HgS.5H_2O$, and red transparent rhomboidal lamellæ of mercuric sulphide. With a certain degree of conc. of the soln., the latter is practically the sole product. It is evident, therefore, that the simple sulphide, HgS, and the double sulphide, K_2S, 5HgS, can be obtained simultaneously as either red or black crystals, but when one is red the other is red, and when one is black the other is black.

According to U. Antony and A. Lucchesi, when an aq. soln. of potassium or sodium gold sulphide, $3M_2S.Au_2S$, is treated with mercuric chloride, a red flocculent precipitate—possibly **gold mercurous sulphide,** $3Hg_2S.Au_2S$—is formed. It is not attacked by acids, but is decomposed by aqua regia. According to C. F. Rammelsberg, an aq. soln. of barium sulphide dissolves black mercuric sulphide; and, according to R. Wagner, cinnabar does not dissolve in that menstruum in the cold, but it does so readily at 40°–50°. J. Knox—*vide supra*—measured the solubility at 25°. The soln. on evaporation furnishes crystals of **pentahydrated barium mercuric sulphide,** $BaS.HgS.5H_2O$. The compound is decomposed by acetic acid with the separation of mercuric sulphide; and when the soln. is treated with an acid, or sat. with hydrogen sulphide, black mercuric sulphide is precipitated. According to J. Petersen, and H. J. Burkart, a **zinc mercuric sulphide,** ZnS.6HgS, occurs as the mineral *guadalcazarite*, but the latter is best regarded as a mixture of metacinnabarite and a little zinc sulphide.

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§ 28. Mercuric Chlorosulphide, Bromosulphide, and Iodosulphide

H. Rose [1] showed that when hydrogen sulphide is passed into a soln. of mercuric chloride, the precipitate, at first white, changes to yellow, then brown, and finally black. The white precipitate is regarded as **mercuric chlorodisulphide,** $2HgS.HgCl_2$, or *mercuric disulphochloride;* and the reaction is symbolized:

$$3Hg<^{Cl}_{Cl} + 2S<^{H}_{H} = 4HCl + Hg<^{S—HgCl}_{S—HgCl}$$

A. Naumann regards mercuric chlorodisulphide as the mercuric salt $Hg(SHgCl)_2$ of *hydrochlorsulphomercuric acid*, HSHgCl; J. S. F. Pagenstecher noted a similar reaction with alkaline sulphides. The continued action of hydrogen sulphide results in the production of black mercuric sulphide, $Hg_3S_2Cl_2+H_2S=2HCl+3HgS$. Instead of using an aq. soln. of mercuric chloride, F. Bezold obtained a similar result by passing hydrogen sulphide into a soln. of mercuric chloride in methyl acetate; M. Hamers, A. Naumann, and E. Alexander used a soln. in ethyl acetate; E. Vogt, a soln. in acetone; and A. Naumann, soln. in ether, benzene, benzonitrile, or methylal; A. Colson also used a benzene soln. According to T. Poleck and C. Goercki, if chlorine is passed into water with freshly precipitated mercuric sulphide in suspension, the latter assumes a bright yellow colour, and finally dissolves. The yellow product has the composition $HgCl_2.2HgS$. Hence mercuric chlorodisulphide represents an intermediate stage in the conversion of mercuric chloride to sulphide, and conversely, T. Poleck and C. Goercki further found that if a mol of mercuric sulphide is digested with a soln. of a mol of mercuric chloride, half the latter remains in soln.; if, however, 2, 3, 4, or 5 mols of the sulphide are employed, no chloride remains in soln., and bright yellow products are formed with $HgS : HgCl_2$ in the molar proportions 2 : 1, 3 : 1, 4 : 1, and 5 : 1 respectively. It is not clear if these products are chemical individuals, more probably they are solid soln. of mercuric sulphide with the disulphochloride. P. Jolibois and P. Bouvier could find no products other than mercuric sulphide, HgS, and the chlorodisulphide, $2HgS.HgCl_2$, as a result of the action of hydrogen sulphide on a dil. soln. of mercuric chloride.

T. Poleck and C. Goercki supposed them to be chemical individuals because they are insoluble in hot and cold water; indeed, they are not changed when heated with water in a sealed tube at 200°. They are not altered by boiling with a soln. of sodium chloride, but in a sealed tube at 190°, they are resolved into their constituents. When heated to 170° with a soln. of potassium iodide, the products are decomposed, $2HgS.HgCl_2+4KI=2HgS+2KCl+K_2HgI_4$. In all cases the red form of mercuric sulphide is obtained; freshly precipitated mercuric sulphide does not become red when treated in the same way; nor is the product obtained by precipitating mercuric chloride with sodium thiosulphate.

Mercuric chlorodisulphide has been produced in numerous other reactions. R. Schneider obtained it by melting in a sealed tube a mixture of 8–10 parts of mercuric chloride with one part of cinnabar or black mercuric sulphide. The powdered mass is washed with water to remove the excess of mercuric chloride. R. Palm made it by the action of a hot soln. of mercuric chloride in excess on sublimed cinnabar, and by adding hydrochloric acid or a soluble chloride to a soln. of mercuric sulphide in one of mercuric acetate. F. Raschig produced it by the action of a soln. of cupric chloride, and J. B. Cammerer by the action of a neutral soln. of ferric chloride on mercuric sulphide; T. Poleck and C. Goercki found that when soln. of sodium thiocarbonate and mercuric chloride are mixed, $HgCl_2+Na_2CS_3+2H_2O=HgS+2NaCl+CO_2+2H_2S$; but if a large excess of dry mercuric chloride is treated with a soln. of sodium thiocarbonate, mercuric chlorodisulphide is produced. The same compound is formed when a soln. of 2 mols of mercuric chloride is mixed with a soln. of one mol of sodium thiosulphate. N. Tarugi obtained mercuric chlorodisulphide by treating a cold neutral soln. of mercuric chloride with thioacetic acid, and also by the action of dil. hydrochloric acid on mercuric thioacetate; and K. Preis, by heating sodium sulphoarsenate with an excess of mercuric chloride.

Mercuric chlorodisulphide is a white friable mass, and when higher proportions of mercuric sulphide are present, the colour is yellow. M. Hamers, and F. Bezold found that the colour darkens on exposure to light. H. Rose noted that when slowly heated in a glass tube, mercuric chlorodisulphide is decomposed into its constituents, both of which sublime, the chloride collecting above the sulphide. M. Hamers, F. Bezold, and E. Alexander noted that the compound can be sublimed with but partial decomposition if rapidly heated. There are some extraordinarily conflicting statements about the properties of this compound. T. Poleck and C. Goercki—*vide supra*—found water had no action, whereas F. Bezold and M. Hamers said that boiling water resolves the complex salt into its components. Again, H. Rose said that it is not dissolved or decomposed by cold or hot, dil. or conc. sulphuric hydrochloric, or nitric acid; that it is decomposed by boiling nitric acid, and that most of the sulphur is oxidized to sulphuric acid; M. Hamers, that with boiling dil. sulphuric, hydrochloric, or nitric acid the salt is decomposed and mercuric chloride passes into soln.; E. Alexander said that although the salt is insoluble in water and in sulphuric acid, it is partly soluble in hydrochloric and nitric acids, and easily soluble in aqua regia; N. Tarugi said that it is soluble only in aqua regia; and E. Vogt that it is insoluble in conc. acids and in aqua regia.

H. Rose showed that when mercuric chlorodisulphide is suspended in water, and treated with hydrogen sulphide, it is converted into black mercuric sulphide; it is also blackened by soln. of alkali hydroxides, or carbonates, forming, according to M. Hamers, mercuric oxide and sulphide, and R. Palm said that a soln. of potassium cyanide extracts the oxide and leaves the sulphide. The carbonates act much more slowly than the hydroxides at ordinary temp. E. Vogt found that when heated with calcium oxide, all the mercury is expelled. H. Rose showed that when heated in a current of chlorine gas, sulphur and mercuric chlorides are formed: $2HgS.HgCl_2+3Cl_2=S_2Cl_2+3HgCl_2$. For the action of a soln. of sodium chloride, and of potassium iodide, *vide supra*.

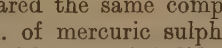
In addition to T. Poleck and C. Goercki's $3HgS.HgCl_2$, $4HgS.HgCl_2$, $5HgS.HgCl_2$, a number of other sulphochlorides or chlorosulphides has been reported, but their individuality has not been established. For example, R. E. Hughes obtained a greenish-yellow precipitate by the action of hydrogen sulphide on a soln. of mercuric chloride in absolute

alcohol. This has a composition approximating to $HgS.HgCl_2$. C. Barfoed reported a yellow product, $12HgS.5HgCl_2$, to be formed by the action of dil. hydrochloric acid on the compound of mercuric nitrate with mercuric sulphide. He assumes this to be a mixture of $2HgS.HgCl_2$ with $3HgS.HgCl_2$. F. Bodroux reported $Hg_2S_5.HgCl_2$ to be formed by the action of calcium polysulphide on an excess of cold soln. of mercuric chloride. F. Capitaine said that a compound, Hg_2SCl_4, is formed when an intimate mixture of mercuric chloride and sulphur is heated; and by the action of sulphur chloride, SCl_2, on mercurous chloride. J. E. Gilpin said that the same compound is produced by heating a mixture of mercuric chloride and arsenic pentasulphide in a retort—arsenic trichloride first sublimes.

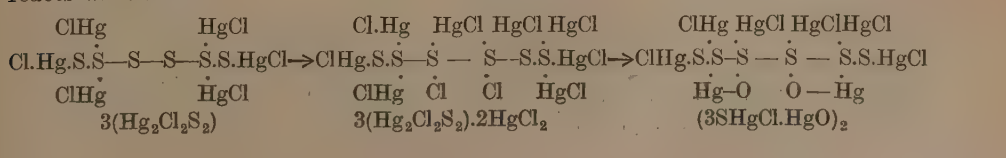
According to G. Franceschi, the addition of a few drops of an alcoholic soln. of hydrogen sulphide to an alcoholic soln. of mercuric bromide produces a slight milkiness: $H_2S+2HgBr_2=2HgBr+S+2HBr$; when more of the hydrogen sulphide soln. is added, the canary-yellow bromodisulphide is formed, $H_2S+6HgBr+3S=2(2HgS.HgBr_2)+2HBr$; and if an excess of the hydrogen sulphide soln. is added, black mercuric sulphide is formed: $H_2S+2HgS.HgBr_2=3HgS+2HBr$. H. Rose, R. Palm, A. Naumann, M. Hamers, and F. Bezold obtained similar results by using a soln. of mercuric bromide in place of the chloride. The product is **mercuric bromodisulphide,** $2HgS.HgBr_2$, or $Hg(S.HgBr)_2$.

H. Rose digested mercuric iodide with an insufficient quantity of potassium sulphide, and obtained a yellow powder taken to be **mercuric iodosulphide,** $HgS.HgI_2$. C. F. Rammelsberg obtained a similar product by dissolving mercuric oxide in a hydrochloric acid soln. of mercuric iodide containing a little hydrogen sulphide; and A. Kekulé, by diluting a soln. of mercuric hydroiodide, sat. with hydrogen sulphide. R. Palm obtained a fiery orange-coloured iodosulphide by the action of a soln. of mercuric iodide on cinnabar. This product was not analyzed. F. Bezold obtained **mercuric iododisulphide,** $2HgS.HgI_2$, by passing dry hydrogen sulphide into a soln. of mercuric iodide in methyl acetate; and M. Hamers used ethyl acetate. R. Palm prepared the same compound by adding hydriodic acid or an alkali iodide to a soln. of mercuric sulphide in one of mercuric acetate. G. Franceschi obtained results with mercuric iodide analogous to those obtained with mercuric bromide. H. Köhler obtained a yellow product which was thought to be **mercuric chloroiodosulphide,** Hg_2SClI, by the action of hydrogen sulphide on a dil. hydrochloric acid soln. of mercuric chloroiodide, HgClI. O. Förster mixed a soln. of allyl thiocyanate in ammoniacal alcohol, or an ammoniacal soln. of allyl thiocarbamide with a soln. of mercuric and potassium iodides, and obtained a lemon-yellow precipitate, **mercuric amminoiododisulphide,** $2HgS.HgI_2.NH_3$, which becomes orange-yellow when dried in darkness. The product is blackened by exposure to light, or by treatment with potassium cyanide.

P. C. Ray [2] prepared *mercury mercaptide nitrite,*



as a white precipitate by adding a dil. aq. soln. of thiocarbamide to a conc. soln. of sodium mercuric nitrite. When this compound is repeatedly boiled with ethyl iodide, and extracted each time with acetone, it furnishes a yellow granular powder, **mercuric diiododisulphide,** $Hg_2I_2S_2$, which slowly darkens in diffused daylight and more rapidly in sunlight. The reaction is *phototropic*, for the original yellow colour is restored in darkness. P. C. Ray and P. K. Sen prepared the corresponding **mercuric dichlorodisulphide,** $Hg_2Cl_2S_2$, but found that this immediately forms **mercuric hexachlorodioxyhexasulphide,** $(3SHgCl.HgO)_2$. Three mols of mercuric dichlorodisulphide first unite with two mols of mercuric chloride, and the product reacts with water:


ClHg HgCl Cl.Hg HgCl HgCl HgCl ClHg HgCl HgCl HgCl
Cl.Hg.S.S—S—S—S.S.HgCl → ClHg.S.S—S — S—S.S.HgCl → ClHg.S.S–S — S — S.S.HgCl
ClHg HgCl ClHg Cl Cl HgCl Hg–O O—Hg
3(Hg2Cl2S2) 3(Hg2Cl2S2).2HgCl2 (3SHgCl.HgO)2

By treating **mercuric dichloratosulphide,** $Hg(ClO_4)_2.HgS$, prepared by the action of hydrogen sulphide on a soln. of mercuric chlorate, with chlorides, nitrates, or sulphates, G. McP. Smith obtained **mercuric dichlorodisulphide,** $HgCl_2.2HgS$; and **mercuric dinitratodisulphide,** $Hg(NO_3)_2.2HgS$.

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[2] P. C. Ray, *Journ. Chem. Soc.*, **111.** 101, 1917; P. C. Ray and P. K. Sen, *ib.*, **115.** 552, 1919; G. McP. Smith, *Science*, (2), **57.** 447, 1923.

§ 29. Mercurous Sulphate

A sulphate of mercury appears to have been made in the fourteenth century by J. de Roquetaillade,[1] for *cum spiritu vitrioli Romani fit magnum adminiculum, ad congelandum Mercurium in substantia, et facit ipsum album sicut nivem.* The Paracelsian school—Basil Valentine, etc.—applied the term *turpethum minerale, mineral turpeth, mineral turbite, turpeth,* or *turbite* to a basic sulphate, but H. Mynsicht used it for other products, and A. Libavius stated:

> Turpeth, a word of Asiatic (should be Persian) origin and the name given to a preparation from the bark or root of a certain ferulaceous plant (*i.e.* of the reed tribe), has slipped into the nomenclature of chemistry, in all probability because of the similarity of its effects with those of a certain secret preparation of mercury. In order to prevent confusion of this latter with the vegetable medicine, the word " mineral " has been added.

A. F. de Fourcroy and L. J. Thénard [2] spoke of three sulphates of mercury, *le sulfate neutre* (mercurous sulphate), *le sulfate avec excès d'acide* (mercuric sulphate), and *le sulfate avec excès d'oxyde* (basic mercuric sulphate). In the dismantling of a mercury furnace at Idria a crust, filled with geodes of small pellucid crystals of **mercurous sulphate,** Hg_2SO_4, was found in the brickwork by G. Seyfriedsberger. Dil. sulphuric acid has scarcely any action on mercury in the cold, but the boiling conc. acid forms sulphur dioxide and mercurous sulphate, Hg_2SO_4, if the mercury is in excess, and mercuric sulphate, $HgSO_4$, if the acid is in excess—*vide* C. Baskerville and W. H. Miller for the action of sulphuric acid on mercury. If two parts of mercury be heated with one to two parts of sulphuric acid until over half is converted into a solid salt, and the mercury and sulphuric acid poured off, mercurous sulphate remains; this is washed with a little cold water. If the mixture has been evaporated to dryness, the product is a mixture of mercurous and mercuric sulphates; if two parts of mercury have been used to one of acid, some free mercury remains; the mercurous salt is gradually converted to the mercuric salt by the hot acid. It is troublesome to prepare mercurous sulphate free from mercuric sulphate by this process, and E. Divers and T. Shimidzu prepared it in the cold by leaving together mercury and fuming sulphuric acid rich in trioxide in a covered and cool vessel. When the metal has all disappeared, the uncovered vessel is left in a warm place to expel the last portions of the sulphur trioxide. It is desirable so to apportion the acid as

to have as little of the trioxide left unconsumed as possible, so that where the mercury taken has proved much too small, more had better be added, still avoiding excess. The product needs only to be transferred to water and washed to be ready for use. F. E. Smith prepared mercurous sulphate by a similar process. H. S. Carhart and G. A. Hulett electrolyzed dil. sulphuric acid (1 : 6) over a layer of mercury which serves as anode, while a platinum wire served as cathode ; the current density was 0·1 amp. per sq. cm. A similar process was used by G. A. Hulett, H. von Steinwehr, F. A. Wolff, A. Brochet and J. Petit, and G. Maneuvrier and J. Chappius.

L. A. Planché prepared mercurous sulphate by triturating a mixture of 18 parts of mercuric sulphate, 6 of water, and 11 of mercury. R. J. Kane prepared mercurous sulphate by treating a soln. of mercurous nitrate with sulphuric acid or sodium sulphate, and washing the precipitate with water. G. A. Hulett dropped an acidified soln. of mercurous nitrate with constant stirring into 1–6 per cent. sulphuric acid ; F. E. Smith, A. de Schulten, R. Varet, and H. von Steinwehr used similar processes. H. Rose triturated crystallized mercurous nitrate with sodium sulphate and dissolved out the sodium nitrate with water. G. Denigès obtained mercurous sulphate by the action of formaldehyde on mercuric sulphate. The reduction proceeds slowly in the cold, rapidly when heated.

C. J. J. Fox recommended purifying commercial mercurous sulphate by heating it with dil. sulphuric acid and pure mercury for some days in a sealed tube or closed flask at 120°–150°. The mixtures should be frequently shaken. The liquid is decanted off, and the solid triturated in a mortar with dil. sulphuric acid two or three times, and then many times with a sat. soln. of cadmium sulphate. The product is then washed with water in a suction funnel. H. S. Carhart has also described the purification of mercurous sulphate for use in Weston's or Clark's standard or normal cells.

Mercurous sulphate appears as a white crystalline powder, which consists of minute monoclinic prisms. G. Seyfriedsberger[3] thought that the **crystals** he found in the Idrian furnace were rhombic, but A. de Schulten showed that they are monoclinic, with axial ratios $a : b : c = 0{\cdot}9002 : 1 : 1{\cdot}4086$, and $\beta = 91° 45'$. G. Seyfriedsberger's specimen had a **specific gravity** 8·353 at 21°/19° ; and A. de Schulten's sample 7·121 at 15° ; while L. Playfair and J. P. Joule gave 7·560 at 3·9°. According to J. Traube, the sp. gr. of a 0·070 per cent. soln. is 0·99985 at 15°, and the **molecular solution volume** is 12·6. In studying the **action of heat,** J. L. Gay Lussac found that the salt fuses to a deep reddish-brown liquid at a dull red heat and immediately decomposes into sulphurous acid, oxygen, and mercury, together with a little sulphuric acid. G. A. Städeler found that the fused mass freezes to a white crystalline solid. E. Cohen and co-workers found the **specific heat** to be 0·0640 at 18·5°–22·5°, and the **molecular heat** 31·83. H. Schottky found the mol. ht., C, to be 30·94 ; and the values at low temp., determined by F. Pollitzer, were 16·74 at −190° ; 17·15 at −188° ; 26·1 at −74° ; and 25·9 at −70°. According to R. Varet, the **heat of formation** is $2Hg_{liq.} + 2O_{2gas} + S_{solid} = Hg_2SO_4 + 175$ Cals. ; and $HgSO_{4solid} + Hg_{liq.} = Hg_2SO_4 + 9{\cdot}9$ Cals. A. de Schulten found mercurous sulphate has a positive **double refraction.** J. A. Wilkinson stated that mercurous sulphate has a yellow **fluorescence** under the influence of the cathode rays, and there is also a yellow light emitted when the salt is formed by electrolysis. G. A. Städeler showed that mercurous sulphate becomes grey under the action of light, probably with the simultaneous formation of mercuric sulphate, and H. S. Carhart found the darkened sulphate gives too high an e.m.f. when used in Weston's standard cell, although S. Skinner said the change is so small as to have a negligible effect on Clark's standard cell. According to S. Skinner, mercurous sulphate is also darkened by exposure to **ultra-violet rays,** sunlight, and the light from the electric arc, as well as to **radium radiations ;** the darkening is independent of the presence of air ; he does not think that the darkening is due to the production of mercury and a mercuric salt, but he believes that a dark sub-salt or a polymeric form may be produced. F. E. Smith said that the **depolarizing effect** of mercurous

sulphate is independent of its mode of preparation, and H. von Steinwehr added that the observed irregularities are dependent on differences in the grain-size of the salt. G. A. Hulett, and P. J. H. van Ginneken have studied the depolarizing action of mercurous sulphate—*vide* standard cells.

The action of water on mercurous sulphate ; basic mercurous sulphates.—The solubility of mercurous sulphate in **water** is small. C. R. A. Wright and C. Thompson [4] found 0·47 grm. is dissolved per litre at 18° ; N. T. M. Wilsmore, 0·39 grm. per litre ; and M. Barre found with Hg_2SO_4 as the solid phase 100 grms. of a sat. soln. contained :

	16·5°	33°	50°	75°	100°
Hg_2SO_4 . . .	0·055	0·060	0·065	0·074	0·092 grm.
H_2SO_4 . . .	0·008	0·018	0·037	0·063	0·071 ,,

J. L. Proust, and M. Donovan supposed the dirty yellow mass obtained by the long-continued action of boiling water on mercurous sulphate is a basic mercurous sulphate, but H. Rose regarded it as a mixture of mercury and a basic mercuric sulphate. According to R. J. Kane, no basic salt is obtained by treating mercurous sulphate either with cold or with boiling water. According to A. Gouy, mercurous sulphate is decomposed by water with formation of a yellow basic sulphate, **mercurous hydroxysulphate,** $Hg_2O.Hg_2SO_4.H_2O$, which resembles basic mercuric sulphate, but has a marked greenish tinge. Equilibrium is established when the water contains 0·410 grm. of mercury and 0·164 grm. of sulphuric acid per litre. Water which contains 0·08 grm. of sulphuric acid per litre does not convert the normal into the basic salt, and a higher proportion of acid converts the basic salt into the normal. When treated with dil. sulphuric acid, the yellow basic salt becomes white, and is thus readily distinguished from basic mercuric sulphate. M. Barre confirms the formation of the basic sulphate indicated by A. Gouy, but he believes that the action is more complex, because some metallic mercury is formed, which, at 50°, imparts a yellowish-green coloration. A. J. Cox found that the hydrolysis furnishes the oxysulphate, $2Hg_2O.SO_3.H_2O$, or $2Hg(OH).Hg_2SO_4$, or $Hg_2O.Hg_2SO_4.H_2O$. According to G. A. Hulett, the formation of the hydroxysulphate introduces an uncertain factor in the standard cell. The presence of the oxysulphate in aq. soln. is evidenced by the presence of free sulphur acid—*vide* M. Barre's data above. A. Gouy said that 0·004 grm. of the basic sulphate dissolves in a litre of water at —20°, and if $\frac{1}{10}N$-sulphuric acid is present, hydrolysis does not occur, and the basic sulphate is converted into the normal sulphate. L. W. Pissarjewsky found that the hydrolysis is smaller in **alcohol** or **glycerol** soln. than in aq. soln. R. J. Kane claimed to have made **dihydrated mercurous sulphate,** $Hg_2SO_4.2H_2O$; but he probably analyzed an imperfectly dried sample.

Many of the so-called basic salts recorded in the literature are mixtures of two or more phases, and the systems analyzed were not always in equilibrium ; and even if the systems were in equilibrium, it was not possible to distinguish between chemical compounds and mixtures of two solid phases because of the absence of any distinguishing test. The phase rule has furnished a light to guide the footsteps of the investigator along this intricate path. Theory has taught the right practice. As a result, many older descriptions of alleged compounds are unsatisfactory. In the special case where basic salts are precipitated from soln. by the hydrolytic action of water—*e.g.* antimony trichloride, bismuth nitrate, mercury salts, etc.—the system will have three components, C, and three phases, P, and since for bivariant systems, $P=C$, it follows from the phase rule (**1.** 8, 5) : (1) If the compositions of the soln. in different experiments are the same while the compositions of the precipitates vary, the soln. will form one phase, and the precipitate will be a mixture of two phases. (2) If the compositions of the soln. in different experiments are different, while the precipitates have the same composition, the precipitate will be a chemical individual. (3) If the compositions of the soln. and of the precipitates vary, the precipitate will be a single phase of variable composition, *i.e.* a solid soln. or mixed crystal.

In the experimental work, soln. of known composition are mixed in flasks and agitated until they are in equilibrium. The flasks are kept the whole time at a uniform temp. and the solid matter allowed to settle. Portions of the liquid are withdrawn for analysis, and the solid is analyzed after it has been separated as free as possible from the mother liquid, say, by press. between porous tiles, by whirling in a centrifuge, etc. Washing the solid may alter the composition of the precipitate.

It is vitally important to have definite evidence that the system is really in a state of equilibrium when the liquid and solid are analyzed. The test for equilibrium is that the composition of the precipitate and soln. is independent of the order in which they are mixed provided that the components are present in eq. amounts, and the temp. are the same. The condition of equilibrium will be the same when approached from both ends; for example, with bismuth nitrate and water, the composition of the oxynitrate will be the same whether bismuth nitrate be mixed with water, or bismuth oxide with dil. nitric acid. In the case of mercurous sulphate and water, A. J. Cox represented the relation between the composition of aq. soln. by the abscissæ, and that of the precipitates by the ordinates. A change in both these variables occurs when the composition of soln. or precipitate changes; and to interpret the results, it is necessary to know only if the composition of the soln. and precipitate changes from experiment to experiment. In representing the composition of soln. and precipitate by a curve, horizontal lines show that compositions of the soln. are variable and of the precipitates constant, and therefore the latter are chemical individuals; vertical lines show that the compositions of the soln. are constant and of the precipitates variable, so that the latter are mixtures of two or more variables; and sloping lines represent the compositions of solid soln. In Fig. 36, the ordinates represent the number of mols of $(H_2, Hg_2)SO_4$ per litre of soln., and the abscissæ, the increased basicity x of the solid phase, *i.e.* $2Hg_2SO_4—xSO_3$. The diagram shows that no basic salt other than $HgO.Hg_2SO_4.H_2O$ is formed by the hydrolysis of mercurous sulphate between 15° and 25°.

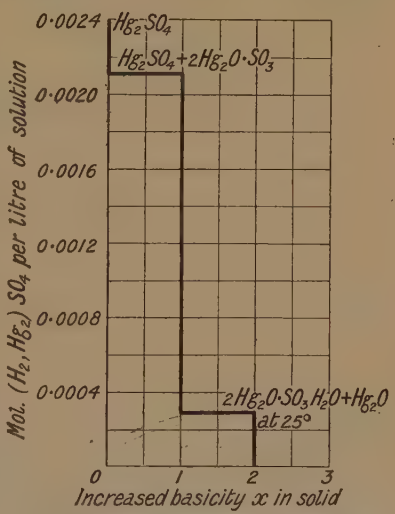

FIG. 36.—Basic Salts of Mercurous Sulphate at 25°.

The chemical reactions of mercurous sulphate.—According to G. A. Hulett, mercurous sulphate in the presence of mercury is not oxidized by exposure to **air**; and H. S. Carhart stated that it can be preserved under dil. sulphuric acid (1 : 6) in darkness. According to S. Hada, moist mercurous sulphate becomes dark brown when exposed to a strong light, and that which has become yellow by treatment with water becomes greenish and then dark brown. The effect is superficial, and may be due to dissociation of the mercurous salt into mercuric salt and water. When heated to 150° in oxygen, with water and a little sulphuric acid, in a sealed tube, about 1·5 per cent. was oxidized. A. Mailfert found that the salt was oxidized by **ozone** to mercuric sulphate and oxysulphate. Mercurous sulphate is abundantly soluble in hot **sulphuric acid,** and part separates out as crystals when the soln. cools, and part is precipitated when water is added to the cold soln. K. Drucker showed that the solubility of mercurous sulphate increases to a maximum with increasing acidity of the soln., thus, with a soln. containing 1·96 grms. H_2SO_4 per litre, 0·41 grm. of salt was dissolved per litre; with 4·90 grms. H_2SO_4 per litre, 0·44 grm. of salt was dissolved; and with 8·04 grms. per litre, 0·40 grm. of salt was dissolved. P. Braham claimed to have made rhombic prisms of **mercurous hydrosulphate,**

$HgHSO_4$, by allowing sulphuric acid with a trace of nitric acid to stand in the cold in contact with mercury for two years. This acid sulphate was found by J. Kendall and A. W. Davidson to be the solid phase in sulphuric acid soln. of this salt, and they found the f.p. of different mixtures to be:

Per cent. Hg_2SO_4	0·68	0·82	1·02	1·18	1·41	1·77	2·17
F.p.	20·0°	27·0°	34·9°	40·1°	47·7°	56·8°	63·3°

Soln. containing over 1·7 molar per cent. $HgSO_4$ rapidly became cloudy on heating owing to the oxidation of mercurous sulphate to the less soluble mercuric salt. The acid sulphate forms a white powder when exposed to the air; at 100° it gives off 5 per cent. of water in 5 mins.; sodium carbonate and potassium hydroxide give black precipitates; and it is attacked by carbon disulphide, ether, and amyl alcohol. K. Drucker found that a litre of a soln. of 34·87 grms. of **potassium sulphate** dissolves 0·45 grm. of mercurous sulphate which is a little less than the 0·58 grm. obtained with water alone. M. Barre's results for the solubility of mercurous sulphate in aq. soln. of potassium sulphate are shown in Table XI, expressed as grams of salt

TABLE XI.—SOLUBILITY OF MERCUROUS SULPHATE IN AQUEOUS SOLUTIONS OF POTASSIUM SULPHATE (Grams of salt per 100 grms. of sat. soln.).

15°			33°			75°		
K_2SO_4	Hg_2SO_4	H_2SO_4	K_2SO_4	Hg_2SO_4	H_2SO_4	K_2SO_4	Hg_2SO_4	H_2SO_4
2·90	0·0475	0·0080	2·94	0·0677	0·0250	3·10	0·1344	0·1684
5·70	0·0703	0·0093	5·68	0·1015	0·0350	5·75	0·2120	0·2135
8·22	0·0912	0·0098	8·30	0·1364	0·0441	8·50	0·2951	0·2514
8·77	0·0994	—	10·70	0·1724	0·0438	13·20	0·4610	0·2503
9·44	0·1080	0·0110	11·90	0·1902	0·0420	17·30	0·6440	0·2225

per 100 grms. of sat. soln. M. Barre stated that there is here no evidence of the formation of a double salt. A. Gouy found that a sat. soln. of **zinc sulphate** or of **cadmium sulphate** decomposes mercurous sulphate much less readily than water, and it dissolves more of the unchanged salt—and according to G. A. Hulett, a sat. soln. of cadmium sulphate dissolves about five times as much salt as does water. G. Bredig and J. W. Brown noted the catalytic oxidation of organic substances in the presence of sulphuric acid and mercurous sulphate. H. W. F. Wackenroder found mercurous sulphate dissolves in dil. **nitric acid,** and is almost wholly re-precipitated by the addition of dil. sulphuric acid. A. F. de Fourcroy obtained a grey product by the action of aq. **ammonia;** and, according to H. Saha and K. N. Choudhuri, conc. ammonia forms $2HgO.(NH_2Hg)_2SO_4.2H_2O$. R. J. Kane believed that oxymercuroammonium sulphate, $\{NH_2(Hg_2OHg_2)\}_2SO_4$, is formed: $4Hg_2SO_4+8NH_3+2H_2O=\{NH_2(Hg_2OHg_2)\}_2SO_4+3(NH_4)_2SO_4$; but L. Pesci, and J. Lefort believed that the product is only a mixture. N. Tarugi also obtained **ammonium mercurous diamminoxysulphate,** $3Hg_2O.2(NH_4)HgSO_4.2NH_3$, by the action of ammonia on ammonium mercurous diamminopersulphate. The white powder is insoluble in cold or hot, dil. or conc. nitric or sulphuric acid, but is soluble in hydrochloric acid.

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§ 30. Mercuric Sulphate

G. Seyfriedsberger[1] obtained a white mass of rhombic crystals of **mercuric sulphate,** $HgSO_4$, in the brickwork of a dismantled mercury furnace at Idria. J. G. Leonhardi, and G. F. Hildebrandt observed that when one part of mercury is heated with $1\frac{1}{2}$ parts of sulphuric acid, and evaporated to dryness, white mercuric sulphate is obtained. M. Geiseler showed that if a smaller proportion of acid is employed the product contains mercury or mercurous sulphate. R. Varet heated 5 parts of mercury with 3 parts of conc. sulphuric acid and a little nitric acid. A. J. Cox evaporated mercury repeatedly with conc. sulphuric acid, and washed the resulting mercuric sulphate with 7*N*-sulphuric acid on a suction funnel—*vide* the action of sulphuric acid on mercury. M. Geiseler evaporated to dryness a mixture of mercuric oxide with about half its weight of sulphuric acid; H. Eissfeldt obtained crystals of mercuric sulphate by treating many mercuric compounds with sulphuric acid—*e.g.* C. A. Cameron evaporated a soln. of basic mercuric sulphate in selenic acid, or basic mercuric selenate in sulphuric acid. K. Kahle purified mercuric sulphate from basic sulphate by treatment with dil. sulphuric acid.

Mercuric sulphate appears as an opaque mass, in white hygroscopic needle-like **crystals,** or, according to C. Hoitsema,[2] in white rhombic plates. L. Playfair and J. P. Joule gave 6·466 for the **specific gravity** at 3·9°; and G. Seyfriedsberger, 5·995 at 21°/19°. According to C. F. Mohr, the **action of heat** on mercuric sulphate is to change the colour from yellow, and then red; and at a bright red-heat, J. L. Gay Lussac found that it decomposes into mercury, mercurous sulphate, and sulphur dioxide.

The **heat of formation,** according to M. Berthelot, is $HgO+H_2SO_4=H_2O+HgSO_4+2{\cdot}6$ Cals., and, according to R. Varet, $Hg_{liq.}+S_{solid}+2O_{2gas}=HgSO_4+166{\cdot}1$ Cals. R. Varet found 4·9 Cals. for the heat of soln. $HgSO_4+4H_2SO_4$.

Mercuric sulphate was found by R. Phillips[3] to be decomposed by **water** into

the basic salt, *turpeth mineral*, $2HgO.HgSO_4$, and a soln. of an acid salt. M. Geiseler obtained a 68 per cent. conversion to the basic sulphate. K. Thümmel showed that the basic salt appears to contain a greater proportion of mercuric oxide, the more water employed in the decomposition of the sulphate. A. Ditte showed that the production of turpeth mineral ceases when the sulphuric acid simultaneously formed : $3HgSO_4+2H_2O \rightleftharpoons 2HgO.HgSO_4+2H_2SO_4$, has a certain conc.—at 12°, 67 grms. SO_3 per litre—if the acid is more or less conc. than this, the normal sulphate is dissolved or decomposed. H. le Chatelier showed that the soln. contains mercuric sulphate, not the basic sulphate ; and that the quantity of acid necessary to prevent the decomposition of a salt increases at first with an increase in the proportion of water ; but it does not increase indefinitely, and tends towards a limit. This limit may be due to a partial dissociation of the hydrates of the acid, or to the comparative insolubility of a particular salt. He further showed that the quantity of free acid required to prevent the decomposition of a salt by water increases indefinitely with the proportion of salt contained in soln. ; and that the decomposition of a dissolved salt increases or decreases with rise of temp. according as the decomposition is endothermal as in the case of antimony trichloride, or exothermal, as in the case of mercuric sulphate. If x represents the quantity of free acid, and y that of mercuric sulphate, $x^{1\cdot58}=4\cdot7y$. Expressing the results in grams per 1000 grms. of water, there is :

15°	Free acid, SO_3	13·1	30·4	39·3	46·7	72·0	98·0
	$HgSO_4$	13·0	47·7	70·7	89·2	197·0	307·0
50°	Free acid, SO_3	8·7	14·0	32·0	41·0	48·0	63·5
	$HgSO_4$	4·9	9·0	28·9	46·6	53·2	68·0
100°	Free acid, SO_3	—	—	38·0	—	63·0	120·0
	$HgSO_4$	—	—	26·6	—	61·0	205·0

R. Varet also found the reaction to be endothermal ; and in water acidified with sulphuric acid, the mercuric sulphate dissolves as an acid salt since with the precipitation 3·6 Cals. more heat are developed than is the case with any other oxysalt of mercury. J. Guinchant, however, believed that the soln. contains the normal salt, because the heat of soln. of mercuric sulphate is independent of the amount of the conc. of the acid, and because conc. sulphuric acid precipitates only the normal salt from acid soln. The fact that M. Geiseler found that a mol. of HgO requires the presence of 4 mols. of H_2SO_4, or, according to R. Phillips, 5 mols. of H_2SO_4, has led to the assumption that the soln. contains *mercuric hydrosulphate*, say, $Hg(HSO_4)_2$. There is no evidence of this. H. Eissfeldt always obtained the normal salt, from soln. in which the mol. ratio was as high as $HgO : H_2SO_4=1 : 5$. A. J. Cox estimated that the soln. must be at least 6·97*N*-H_2SO_4 at 25°, in order that the acid salt may be present. J. Kendall and A. W. Davidson found the f.p. of 0·023, 0·048, and 0·094 per cent. soln. of mercuric sulphate in sulphuric acid to be respectively 36°, 77°, and 127°, and the solid phase to be the normal sulphate.

H. Eissfeldt prepared colourless prismatic crystals of what he regarded as **monohydrated mercuric sulphate,** $HgSO_4.H_2O$, by leaving mercuric sulphate under a layer of cold water until it begins to turn yellow ; but C. Hoitsema said that the basic sulphate $3HgO.2SO_3.2H_2O$ is formed under these conditions. C. Hoitsema, however, did prepare the hydrate by leaving a sulphuric acid soln. of mercuric sulphate, Fig. 37, in a desiccator over sulphuric acid at room temp.

C. Hoitsema, and J. M. van Bemmelen studied the ternary system, $HgO—SO_3—H_2O$, at 25° and 50°, and found that four solid phases, $HgSO_4$, $HgSO_4.H_2O$, $HgO.HgSO_4.2H_2O$, and $2HgO.HgSO_4$, may be present, after 3 hrs.' agitation. At 25°, the first branch of the curve, Fig. 37, has $3HgO.SO_3$ as solid phase as the mol. proportion of HgO increases from 0·33 to 2·0 per cent. and of SO_3 from 1·24 to 4·3 per cent. The curve then cuts another branch where the solid phase is $3HgO.2SO_3.2H_2O$, and the mol. percentage of HgO increases but slightly with increasing content of acid. This curve then cuts that of the solid phase $HgSO_4.H_2O$ with 6·77 mols. per cent. of SO_3 and 2·02 mols. per cent. of HgO, and this phase persists until 8·1 mols. per

cent. of SO_3 and 0·6 mol. per cent. of HgO are present, Fig. 37, when the phase $HgSO_4$ appears. At 50° the phase $HgSO_4.H_2O$ disappears. The curves also indicate that soln. of turpeth mineral, and of mercuric sulphate as solid phase, will

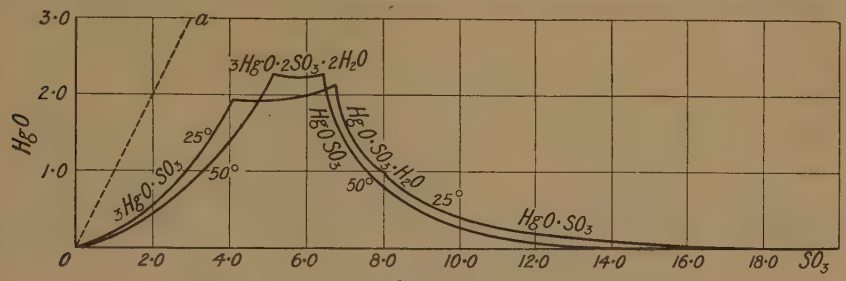


FIG. 37.—The Ternary System, HgO—SO_3—H_2O.

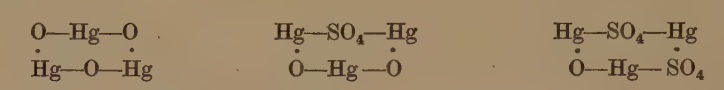
precipitate the solid by warming, but this does not hold for cases in which the solid phase is $3HgO.2SO_3.2H_2O$, where a rise of temp. may cause a transition to either $2HgO.HgSO_4$ or to $HgSO_4$; this is a transition from $HgSO_4.H_2O$ to $HgSO_4$. A line 0*a* equidistant from the two axes (on the same scale) does not cut the $HgSO_4$ curve; this means that $HgSO_4$ is not soluble in water without decomposition.

According to A. Ditte,[4] mercuric sulphate is slightly soluble in **hydrofluoric acid,** but on evaporation, the soln. furnishes mercuric sulphate—there is no sign of the formation of a fluosulphate analogous to the chlorosulphate, $HgSO_4.2HCl$. C. F. Mohr stated that mercuric sulphate does not absorb **hydrogen chloride** at ordinary temp., but when heated, it takes up that gas with avidity, much heat is developed, and some mercuric chloride is sublimed: $HgSO_4+2HCl \rightleftharpoons HgCl_2+H_2SO_4$. The action is reversible so that some unchanged mercuric sulphate remains when the mercuric chloride has been all sublimed. R. J. Kane said that the dry salt absorbs hydrogen chloride, and gives it up again when warmed, when exposed to the air, or when washed with water. C. F. Mohr, and J. B. Hannay also found **hydrochloric acid** reacts with dry mercuric sulphate with a rise of temp. and the formation of mercuric chloride and sulphuric acid. A. B. Prescott found the reaction to be quantitative. According to A. Mailhe, and A. J. Cox, when a mixture of mercuric sulphate and **iodine** is heated there is a slight reaction, and a yellowish-white, hard, crystalline body is formed which is decomposed by water. E. Riegel, and A. Souville have studied the formation of **mercuric sulphatoiodide,** $HgSO_4.HgI_2$. According to K. Brückner, if a mixture of mercuric sulphate and iodine be mixed with water, it immediately becomes red owing to the formation of mercuric iodide—some mercuric iodate is also formed—the water extracts some mercurous and mercuric iodide and sulphate. M. Chateau believes that K. Brückner's sulphato-iodide is really an equilibrium mixture of a basic mercury sulphate, $HgSO_4.HgO$, and iodosulphate, $HgSO_4.HgI_2$, and the iodate, $Hg(IO_3)_2$, in the molar proportions 6 : 6 : 1. When the iodine is replaced by **bromine,** or **chlorine,** oxygen is evolved and mercuric bromide or chloride is formed. Mercuric sulphate is slightly soluble in **hydriodic acid,** and A. Ditte observed no sign of the formation of a compound analogous with $HgSO_4.2HCl$; when the aq. soln. is evaporated, crystals of mercuric iodide appear. When triturated with potassium iodide, C. F. Mohr observed the formation of mercuric iodide and potassium sulphate.

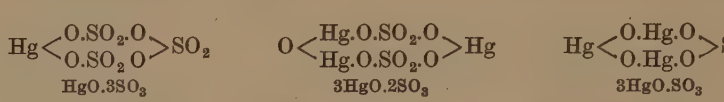
According to A. Violi, when mercuric sulphate is mixed with molten **sulphur,** mercuric sulphide and sulphur dioxide are formed. For the action of **sulphuric acid,** *vide supra*. For silver mercuric sulphate and sulphato-chloride, see silver mercuric nitrate. J. L. Gay Lussac found that when heated with **carbon**—charcoal—mercury, carbon dioxide, and sulphur dioxide are formed. According to C. F. Mohr, **hydrogen cyanide** acts on heated mercuric sulphate, forming mercuric

cyanide and sulphuric acid, and R. Varet said the reaction is complete; according to C. F. Mohr, aq. **hydrocyanic acid** acts similarly and causes a rise of temp.; when the soln. is boiled, mercurous sulphate is deposited, and mercuric sulphate remains in soln. G. Denigès found that the **ethylene** hydrocarbons form a yellow precipitate in acid soln. J. Schröder found mercuric sulphate to be insoluble in **pyridine**; and A. Naumann, that it is likewise insoluble in **benzonitrile.** G. Denigès, C. Oppenheimer, etc., have noted the formation of complexes with a number of organic compounds—thiophene, aldehydes and ketones, etc.

The basic mercuric sulphates.—The hydrolytic action of water on mercuric sulphate and C. Hoitsema's work [5] on the ternary system, $HgO—SO_3—H_2O$, have been previously discussed; the latter shows the existence of two well-defined basic salts at ordinary temp., $3HgO.SO_3$, and $3HgO.2SO_3.2H_2O$, and, according to W. Spring's scheme, these would be referred to the oxide, $(HgO)_3$, and graphically represented:



The basic sulphates, $HgO : SO_3 = 1 : 3$, $3 : 2$, and $3 : 1$, can also be formulated:



The basic sulphate, $3HgO.SO_3$, also called *turpeth mineral*, can be regarded as a salt of orthosulphuric acid, $S(OH)_6$, or H_6SO_6, namely, Hg_3SO_6, *mercury orthosulphate.*

The results of A. J. Cox's application of the phase rule to systems of mercuric sulphate and dil. sulphuric acid are shown in Fig. 38, analogous with Fig. 36 (*q.v.*).

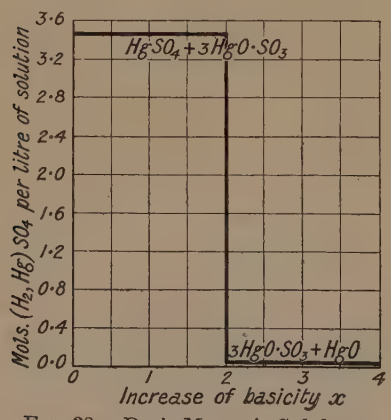


FIG. 38.—Basic Mercuric Sulphates (25°).

The ordinates represent mols of $(Hg_2, Hg)SO_4$ per litre of soln., and the abscissæ the increase x in the basicity of the solid phase from $3HgSO_4—xSO_3$. Only one basic salt, $3HgO.SO_3$, was found corresponding with the minimum acid conc. 0·0013*N*- at 25°. The **mercuric dioxysulphate,** $3HgO.SO_3$, or $HgSO_4.2HgO$, has been long known as *mineral turpeth* or *turpeth.* It was studied by A. F. de Fourcroy, R. J. Kane, R. Phillips, M. Braamcamp and S. Oliva, etc. G. F. Hildebrandt, R. Phillips, A. J. Cox, A. Ditte, and R. Varet described its preparation by the action of water, particularly boiling water, on mercuric sulphate; and C. Hoitsema showed the conditions under which it is stable in dil. sulphuric acid. A. J. Cox showed that if mercuric oxide be shaken some days with an excess of sulphuric acid, when all the mercuric oxide is converted into turpeth, the acid is between 6·87*N*- and 0·00065*N*-; and M. Geiseler obtained an orange-yellow mass resembling turpeth by heating 108 parts of mercuric oxide with 16·2 parts of sulphuric acid and 540 parts of water. M. Geiseler also made it by treating a warm soln. of mercuric nitrate with sodium sulphate. P. C. Ray obtained it by boiling the mother liquor remaining after the preparation of the hemihydrate. A. Mailhe prepared it by the action of mercuric sulphate on cupric hydroxide. W. R. Dunstan and T. S. Dymond prepared a yellow crystalline powder of **hemihydrated mercuric dioxysulphate,** $3HgO.SO_3.\frac{1}{2}H_2O$, or

$HgSO_4.2HgO.\frac{1}{2}H_2O$, from the mother liquids obtained in the preparation of mercuric oxynitrates. Although the yellow mineral turpeth is usually regarded as anhydrous, P. C. Ray said that this compound is the hemihydrate.

P. C. Ray showed that mercuric dioxysulphate may be formed as a lemon-yellow powder or in bright yellow scales; that obtained by the hydrolysis of mercuric sulphate consists of small, yellow tetragonal crystals. R. Watson gave 6·444 and L. Playfair and J. P. Joule 8·319 at 3·9° for the **specific gravity.** R. Watson, and E. J. Houston showed that the greenish-yellow powder becomes red when heated. According to G. F. Hildebrandt, when the anhydrous turpeth is heated it forms a white sublimate, and some mercury is obtained when it is rapidly and strongly heated. P. C. Ray found that when heated to 400°, the basic sulphate gives off mercury and oxygen, forming normal mercuric sulphate, which melts to a brown liquid and sublimes as mercurous sulphate with the evolution of oxygen and sulphur dioxide: $2(HgSO_4.2HgO)=Hg_2SO_4+4Hg+3O_2+SO_2$. R. Varet gave for the **heat of formation,** $3HgO+SO_3=3HgO.SO_3+50{\cdot}58$ Cals., and 9·2 Cals. for the **heat of solution** in sulphuric acid, $3HgO.SO_3+25H_2SO_4$. P. C. Ray also noted the change in the colour of the hemihydrate from yellow to red and brown when heated, and the restoration of the original colour on cooling. The water is, however, given off during the heating. A. Ditte said that the dioxysulphate is insoluble in **water;** A. F. de Fourcroy, that a litre of cold water dissolves 0·05 grm., and a litre of boiling water 1·67 grms.; and C. A. Cameron, that at 100° a litre of water dissolves 0·023 grm. of the dried and 0·031 grm. of the freshly precipitated sulphate. According to T. J. Pelouze, the action of **chlorine** is very slow at ordinary temp., and the result resembles that with mercuric oxide. A. Ditte said that the basic salt is soluble in dil. **hydrochloric acid,** which, according to C. F. Mohr, converts it completely into mercuric chloride and sulphuric acid. P. C. Ray said that the turbidity of the soln. in hydrochloric acid is due to the presence of traces of mercurous chloride. A. Vogel found that sulphurous acid dissolves turpeth, and the soln. becomes turbid owing to the separation of mercurous sulphate, and if the soln. be boiled, some mercury is formed. For H. le Chatelier, J. Guinchant, and R. Varet on the action of sulphuric acid, *vide supra*, Figs. 36-38. According to A. Ditte, if x denotes the weight of H_2SO_4, and y that of mercuric oxide present in the form of $3HgO.SO_3$, $y=0{\cdot}508x-1{\cdot}776$. P. C. Ray, and A. Ditte noted the solubility of the basic sulphate in dil. **nitric acid**, and also in **acetic acid.** M. Donovan said that the basic sulphate gives up all its acid to a soln. of **potassium hydroxide.**

C. Hoitsema prepared colourless, monoclinic plates of dihydrated **mercuric monoxydisulphate,** $2HgSO_4.HgO.2H_2O$, or $3HgO.2SO_3.2H_2O$, by the action of sulphuric acid on mercuric oxide; the conc. of the acid has been indicated previously—*vide supra*. Its presence was also indicated by the previous work of J. M. van Bemmelen. The air-dried compound loses water very slowly at 100°, but rapidly at 125°, forming an orange-yellow powder. The heat of soln. is probably negative. There is a doubt about the **mercuric monoxysulphate,** $2HgO.SO_3$, or $HgSO_4.HgO$, reported by A. Mailhe to be formed by the action of nickel hydroxide or nickel carbonate on a soln. of mercuric sulphate. Similar remarks apply to the **mercuric monoxytrisulphate,** $4HgO.3SO_3$, or $3HgSO_4.HgO$, reported by W. T. Hopkins, and N. Athanasesco—the former by the action of nitric acid on anhydrous turpeth, and the latter by heating a mixture of sodium sulphate with an acidified soln. of mercuric nitrate in a sealed tube at 250°. The dark yellow rhombohedral crystals are said to be decomposed by water with the separation of turpeth. C. Hoitsema regards it as a mixture of turpeth and mercuric sulphate.

The sulphobasic mercuric sulphates.—Some complexes of mercuric sulphide and sulphate have been reported—**mercuric sulphatosulphides**—with $HgS:HgSO_4$ in the mol. ratio 1 : 3, 1 : 2, 2 : 1, and 3 : 1, as well as some *mercuric oxysulphatosulphides*, $2HgS.3HgSO_4.HgO.4H_2O$, and $HgS.HgSO_4.HgO$. W. Spring [6] regards sulpho-sulphates as derivatives of

$$S<^{Hg.S.Hg}_{Hg.S.Hg}>S \qquad S<^{Hg.S}_{Hg.S}>Hg$$

in which SO_4-radicles may replace the sulphur radicles. Thus

$$S<^{Hg.S.Hg}_{Hg.S.Hg}>SO_4 \qquad S<^{Hg.SO_4.Hg}_{Hg.SO_4.Hg}>SO_4$$

$3HgS.HgSO_4$ $\qquad$ $HgS.3HgSO_4$

The oxysulphates are similar, but here oxygen replaces sulphur. The yellow amorphous precipitate which H. W. F. Wackenroder obtained by adding mercurous nitrate to an aq. soln. of tetrathionic acid was shown by W. Spring to be **mercuric sulphatotrisulphide,** $3HgS.HgSO_4$, or $Hg_4S_4O_4$. The result is not satisfactory if the tetrathionic acid be poured into an aq. soln. of mercurous nitrate. Presumably mercurous tetrathionate, $Hg_2S_4O_6$, is first formed: $H_2S_4O_6+Hg_2(NO_3)_2=Hg_2S_4O_6+2HNO_3$; and immediately hydrolyzed by the water: $2Hg_2S_4O_6+3H_2O=Hg_4S_4O_4+2H_2SO_4+H_2SO_3+S$. The yellow precipitate was washed with carbon disulphide, and dried. N. Tarugi made the same compound by treating mercuric ethyl thiocarbonate, $Hg(CH_3COS)_2$ with dil. sulphuric acid. According to W. Spring, the sp. gr. of the yellow powder at 20° is 6·4159, and the mol. vol., 154·6. It is stable up to 120°, but above that temp. it blackens, and decomposes, giving off white fumes. If the salt is contaminated with a little tetrathionic acid, it begins to decompose at about 50°. The purified salt is stable in light, but if contaminated with tetrathionic acid, it blackens, forming mercuric sulphide and sulphate. The salt is insoluble in water, but the yellow powder becomes darker in boiling water, and the filtrate is free from mercury, but contains sulphuric acid; the product remaining after treatment with boiling water is mercuric trioxysulphide, HgO.3HgS. Alkalies, iodides, and substances with an alkaline reaction, like the carbonates, form black mercuric sulphide, and this the more quickly the higher the temp. The salt is also blackened by hydrogen sulphide. It resists the action of acids excepting conc. tetrathionic acid, which partially dissolves it, and hot nitric acid converts it into $HgS.3HgSO_4$. It is soluble in aqua regia, or a soln. of bromine in hydrochloric acid. When boiled with a soln. of barium nitrate it forms mercuric sulphide, barium sulphate, etc. The amount of heat evolved when this body is treated with sodium sulphide is taken to mean that it is not a mere mixture of mercuric sulphide and sulphate, but is rather a definite compound. When the sulphatotrisulphide is warmed to 95°–100° with nitric acid of moderate conc., it forms **mercuric trisulphatosulphide,** $HgS.3HgSO_4$, as a white powder, which is coloured yellow and then black by sodium hydroxide, and which is insoluble in acids and in aqua regia.

R. Palm reported the formation of white **mercuric disulphatosulphide,** $HgS.2HgSO_4$, by mixing freshly precipitated mercuric sulphide in a conc. soln. of mercuric acetate with sulphuric acid or an alkali sulphate; and he added that a similar compound, but red in colour, is formed by the action of a warm soln. of mercuric sulphate on cinnabar. C. Barfoed also reported the formation of **mercuric sulphatodisulphide,** $2HgS.HgSO_4$, by the action of warm sulphuric acid on mercuric sulphonitrate. G. McP. Smith obtained this compound by the action of a sulphate on mercuric diperchloratosulphide.

H. Rose obtained a product, **mercuric oxysulphosulphate,** $HgS.HgO.HgSO_4$, by treating an aq. soln. of mercuric sulphate with insufficient hydrogen sulphide for complete decomposition. The white precipitate becomes yellow by washing, and J. Jacobson said that it remains white if washed with cold water and dried in the water-bath, but if washed with boiling water it becomes yellow. According to K. Estrup, if a soln. of mercuric sulphate, made by dissolving 10 grms. of yellow mercuric oxide in 10 c.c. of conc. sulphuric acid and 40 c.c. of water, is shaken with one-fourth its vol. of carbon disulphide, and allowed to stand several weeks, white hexagonal plates are formed, which, after washing with dil. sulphuric acid, alcohol, and ether, have the composition $4HgO.2HgS.3SO_3.4H_2O$, or $2HgS.HgO.3HgSO_4.4H_2O$, or **tetrahydrated mercuric oxydisulphotrisulphate,** and he

gave the graphic formula $(HO.Hg.SO_4.Hg.S.Hg)_2SO_4$. E. Bijlmann made it by dissolving 10 grms. of yellow mercuric oxide in 10 c.c. of conc. sulphuric acid mixed with 10 c.c. of water. When this compound is boiled with a soln. of potassium iodide, mercuric sulphide is precipitated and 2 eq. of alkali are set free. The compound is coloured yellow after standing some time in contact with water.

Mixed salts of mercuric sulphate.—C. Baskerville and F. W. Miller[7] prepared a crystalline powder, which they regarded as **mercurosic sulphate,** $Hg_2SO_4.HgSO_4$, by digesting mercury with conc. sulphuric acid for 2 hrs. at 150°. The precipitate is washed with 95 per cent. alcohol. T. Brooks obtained what he regarded as **mercurosic oxysulphate,** $Hg_2O.HgO.HgSO_4$, or $Hg_2O.2HgO.SO_3$, by warming mercuromercuric nitrate with sodium sulphate. The product is insoluble in cold water, and it is decomposed by hydrochloric acid. There is nothing to show that these products are chemical individuals. Mercuric sulphate was found by C. Baskerville to form **mercuric hydrochlorosulphate,** $HgSO_4.HCl$, by evaporating to dryness a mixture of 20 grms. of mercuric sulphate and 20 c.c. of conc. hydrochloric acid, and then subliming the product at 240°. The sublimate is not attacked by hydrochloric acid, and but slightly by nitric acid. A. Ditte made **mercuric dihydrochlorosulphate,** $HgSO_4.2HCl$, by passing dry hydrogen chloride through a tube containing powdered mercuric sulphate at a temp. sufficient to volatilize any mercuric chloride which may be formed ; also by evaporating a mixture of mercuric sulphate and hot conc. hydrochloric acid to dryness ; and also by subliming a mixture of eq. proportions of mercuric sulphate and chloride. The white product is soluble in water without decomposition ; it is soluble in hot sulphuric acid. C. Baskerville made monoclinic crystals of the hydrate, $HgSO_4.2HCl.H_2O$, by heating a mixture of eq. quantities of mercuric chloride and monohydrated mercuric sulphate. A. Ditte similarly prepared **mercuric dihydrobromosulphate,** $HgSO_4.2HBr$; but he could not obtain the corresponding compound with hydrogen iodide. A. Ditte also made white crystals of a basic salt, $HgSO_4.2HgO.6HBr$, by the action of dry hydrogen bromide on cooled mercuric oxysulphate, $HgSO_4.HgO$; and by evaporating to dryness a soln. of mercuric dioxysulphate, $HgSO_4.2HgO$, in hot hydrobromic acid. The compound decomposes when heated with water, forming mercuric bromide, and mercuric dihydrobromosulphate.

A. Ditte prepared white crystals of **mercuric dioxyhexahydrochlorosulphate,** $2HgO.HgSO_4.6HCl$, by the action of hydrogen chloride on turpeth mineral, and by evaporating to dryness a soln. of turpeth mineral in conc. hydrochloric acid. When heated the product is decomposed into water, mercuric chloride, and $HgSO_4.2HCl$. The corresponding **mercuric dioxyhexahydrobromosulphate,** $2HgO.HgSO_4.6HBr$, was prepared in a similar manner. According to A. Ditte, if a mixture of mercuric iodide and sulphuric acid be heated, sublimation begins at 200°, and iodine is given off ; on cooling, a mass of crystals of a double salt is possibly formed. This product melts to a yellow liquid ; it is coloured yellow and then red by cold water, and decomposed by hot water. A. Souville, and E. Riegel studied this reaction, and it has been assumed, without proof, that **mercuric iodosulphate,** $HgSO_4.HgI_2$, is formed. A. Ditte prepared white silky needles of **mercuric iodotrisulphate,** $HgI_2.3HgSO_4$, by heating mercuric iodide with fuming sulphuric acid, or, less readily, with ordinary sulphuric acid. The salt can be recrystallized from sulphuric acid ; it melts to a yellow liquid which solidifies on cooling to a white fibrous mass ; it is decomposed by water, forming mercuric iodide and turpeth mineral. A. Ditte also prepared five different double salts of mercuric sulphate and iodide by the action of sat. soln. of mercuric sulphate in sulphuric acid of different conc. upon mercuric iodide ; **mercuric iodotetrasulphate,** $HgI_2.4HgSO_4.15$ or $18H_2O$, from a 41·1 per cent. sulphuric acid soln. ; brilliant white needles of **mercuric oxyiodotrisulphate,** $HgI_2(3HgO.2SO_3)(HgO.SO_3).10H_2O$, or $HgI_2.HgO.3HgSO_4.10H_2O$, from 37·5 per cent. acid soln. ; white nodular crystalline masses of **mercuric iododioxytetrasulphate,** $HgI_2.2(2SO_3.3HgO).10H_2O$, or $HgI_2.2HgO.4HgSO_4.10H_2O$, from 28·5 per cent. acid soln. ; rose-coloured crystals of **mercuric**

diiodotrioxyhexasulphate, $2HgI_2.3(2SO_3.3HgO).10H_2O$, or $2HgI_2.3HgO.6HgSO_4.10H_2O$, from a 16·6 per cent. acid soln.; and white crystals of **mercuric iodo-oxydisulphate,** $HgI_2.(2SO_3.3HgO)$, or $HgI_2.HgO.2HgSO_4$, from a 9 per cent. acid soln. K. Brückner reported **mercuric hexaiodoiodatohexoxydodecasulphate,** $6HgI_2.6(2SO_3.3HgO).Hg(IO_3)_2$, or $6HgI_2.6HgO.12HgSO_4.Hg(IO_3)_2$, by shaking together a mixture of 600 grms. of mercuric sulphate, 800 grms. of water, and 50 grms. of iodine; and by the action of an alcoholic soln. of potassium iodide on basic mercuric sulphate. The microcrystalline product is decomposed by water and dil. acids.

C. H. Hirzel [8] prepared colourless monoclinic crystals of dihydrated **potassium trimercuric sulphate,** $K_2SO_4.3HgSO_4.2H_2O$, by dissolving a mol of mercuric sulphate in hot sulphuric acid, and adding potassium sulphate until the precipitate first formed re-dissolves. The soln. is treated with boiling water until a permanent turbidity is produced, and the whole is allowed to cool slowly. According to B. Finzi, when a boiling soln. of silver sulphate (sat. in the cold) is treated with yellow mercuric oxide until no more dissolves, and the filtered soln. allowed to stand a few days, pale-yellow rhombic tablets of **silver mercuric oxysulphate,** $Ag_2SO_4.HgO$, are deposited.

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§ 31. Ammoniacal, Hydrazine, and Hydroxylamine Mercuric Sulphates

E. C. Franklin and C. A. Kraus [1] found mercuric sulphate to be insoluble in liquid ammonia; but it is soluble in aq. ammonia. N. A. E. Millon prepared a compound with the empirical formula $Hg_3N_2H_6O_2SO_4$, by saturating 90 c.c. of conc. and cold aq. ammonia with mercuric sulphate, and leaving the soln. in an atm. of ammonia over quicklime for some months. The prismatic crystals which formed were dried over sulphuric acid. L. Pesci was unable to prepare this sulphate, but obtained ammonia turpeth instead; N. A. E. Millon considered it to be *oxytrimercuridiammonium sulphate*, $3HgO.SO_3.2NH_3$; but E. C. Franklin regarded it as **mercuric diamminodioxysulphate,** $Hg(NH_3)_2SO_4.2HgO$, or as *hydrated mercuriammonium mercurihydroxysulphatoamide*, $NH_2Hg.SO_4.HgNHHgOH + H_2O$. N. A. E. Millon prepared prismatic crystals of what he regarded as *oxydimercuriammonium sulphate*, $2HgO.SO_3.2NH_3$, by evaporating a sat. soln. of mercuric sulphate in conc. aq. ammonia, in an atm. of ammonia. L. Pesci obtained only ammonia turpeth by following N. A. E. Millon's directions. E. C. Franklin regards this product as **mercuric diamminomonoxysulphate,** $Hg(NH_3)_2SO_4.HgO$, or as *hydrated mercuriammonium sulphate*, $(NH_2Hg)_2SO_4.H_2O$.

N. A. E. Millon likewise prepared **mercuric diamminosulphate,** $Hg(NH_3)_2SO_4$, by saturating aq. ammonia with mercuric sulphate and evaporating to dryness over sulphuric acid. L. Pesci followed these directions and obtained a product of the same composition which he assumed to be a mixture. O. Schmieder prepared fine crystals of **monohydrated mercuric diamminosulphate,** $Hg(NH_3)_2SO_4.H_2O$, by evaporating a sat. soln. of precipitated mercuric oxide in a cold soln. of ammonium sulphate until a crop of crystals appeared; if the soln. be hot during the evaporation, a basic salt appears. L. Pesci followed O. Schmieder's directions, and obtained a compound of this same composition to which he assigned the formula $(NHg_2)_2SO_4.3(NH_4)_2SO_4.4H_2O$. The crystals are stable in air, and, according to L. Pesci, rapidly become opaque when confined over sulphuric acid. The compound is white at 90°, but at 115° it becomes reddish and loses all its water. When heated in a glass tube, water and ammonia are first evolved; mercury and a yellow sublimate then appear—the latter is white when cold—the reddish-brown residue melts with bubbling and evolution of sulphur dioxide; and at a still higher temp., all is volatilized. According to O. Schmieder, when the compound is treated with a very small proportion of cold water, a complex compound which L. Pesci symbolized $(NH_4)_2SO_4.7(NHg_2)_2SO_4.12H_2O$—*vide infra*—is formed; and with boiling water ammonia turpeth—*vide infra*—appears. A soln. of potassium hydroxide furnishes a basic salt and ammonia even at ordinary temp., and with a boiling soln., the yellow compound first produced is gradually converted into mercuric oxide. The compound is easily soluble in aq. soln. of ammonium sulphate

or ammonium chloride ; in dil. or conc. hydrochloric acid ; and in very dil. nitric or sulphuric acid ; but it is not soluble in conc. nitric acid, and conc. sulphuric acid decomposes it, forming mercuric and ammonium sulphates. Hydrogen sulphide converts it completely into mercuric sulphide and ammonium sulphate.

K. A. Hofmann and E. C. Marburg obtained a pulverulent precipitate of **mercuric hydrazinosulphate,** $HgSO_4.N_2H_4$, by adding hydrazine sulphate to a soln. of mercuric nitrate. M. Adams made **mercuric dihydroxylaminosulphate,** $HgSO_4.2NH_2OH.H_2O$, by shaking freshly precipitated mercuric oxide, or dry mercuric sulphate with a cold 10 per cent. soln. of hydroxylamine sulphate. An excess of mercuric oxide is to be avoided. The crystals are repeatedly washed with water, and dried over phosphorus pentoxide. The compound is stable in darkness, but changes colour in light. It decomposes rapidly at 55° ; and it is decomposed by cold water, being coloured first reddish-yellow, and finally black. It is stable under water containing some sulphuric acid or hydroxylamine sulphate.

A. F. de Fourcroy [2] found that soln. of a mercuric sulphate—not the nitrate or chloride—give a white precipitate with ammonium sulphate. G. C. Wittstein stated that a soln. of mercuric oxide in a cold aq. soln. of ammonium sulphate is not precipitated by aq. ammonia ; and he added that if mercurous oxide be used, heat is necessary for the dissolution and some mercury is precipitated. C. H. Hirzel dissolved a mol of mercuric sulphate in hot sulphuric acid, and added a mol of ammonium sulphate ; the precipitate first formed redissolved, boiling water was added, and the mixture cooled slowly when monoclinic prisms of **dihydrated ammonium trimercuric sulphate,** $(NH_4)_2SO_4.3HgSO_4.2H_2O$, separated out. The double salt is much dissociated in aq. soln. since H. C. Jones and K. Ota found that the conductivity very nearly corresponds with the value calculated from that of the single salts.

C. Kosmann prepared what he regarded as **mercuric ammonium sulphatochloride,** $2HgSO_4.HgCl_2.2NH_4Cl$, by boiling mercuric chloroamide, NH_2HgCl, with sufficient water, acidulated with sulphuric acid, for complete soln. The liquid is evaporated on a water-bath for crystallization : $4NH_2HgCl+4H_2SO_4=HgSO_4+(NH_4)_2SO_4+2NH_4Cl.2HgSO_4.HgCl_2$. The crystals are dried by press. between filter-paper. They are decomposed by water ; potassium hydroxide liberates ammonia ; and ether extracts mercuric chloride.

P. C. Ray obtained a white crystalline powder of **monohydrated dimercuriammonium sulphate,** $(NHg_2)_2SO_4.H_2O$, by heating dimercuriammonium nitrite with dil. sulphuric acid slowly up to the b.p. The product is soluble in hydrochloric acid. By warming Millon's base with dil. sulphuric acid, C. F. Rammelsberg, and L. Pesci obtained **dihydrated dimercuriammonium sulphate,** $(NHg_2)_2SO_4.2H_2O$, as a pale yellow powder, and L. Pesci obtained octahedral crystals by adding mercuric sulphate to 70–100 c.c. of cold conc. aq. ammonia until no more dissolved, and evaporating the soln. for crystals. L. Pesci prepared a double salt, **dodecahydrated ammonium heptadimercuriammonium sulphate,** $(NH_4)_2SO_4.7(NHg_2)_2SO_4.12H_2O$, which some regard as mercuriammonium oxydimercuriammonium sulphate, *q.v.* This salt becomes anhydrous when heated to 115°. H. Saha and K. N. Choudhuri obtained **dihydrated mercuriammonium oxysulphate,** $2HgO.(NH_2Hg)_2SO_4.2H_2O$, by dissolving mercurous sulphate in aq. ammonia, and evaporating the filtered soln. over conc. sulphuric acid.

Prismatic crystals of another ammonium dimercuriammonium sulphate, $14(NH_4)_2SO_4.5(NHg_2)_2SO_4.16H_2O$, were prepared by L. Pesci by adding mercuric sulphate to aq. ammonia of sp. gr. 0·906 until no more dissolved ; mixing the filtered soln. with an equal vol. of an aq. soln. of ammonia sat. at 0° ; and allowing the mixture to stand 24 hrs. This salt becomes anhydrous at 115°–125°. It loses ammonium sulphate when treated with cold water, and forms $(NH_4)_2SO_4.7(NHg_2)_2SO_4.12H_2O$, and finally the sulphate of Millon's base. The salt is soluble in aq. ammonia. The aq. soln. gives a precipitate of mercuric sulphide when treated with hydrogen sulphide, and a neutral soln. of ammonium sulphate remains. E. C. Franklin rearranges the symbols in the formula of the hydrate so as to form $HgO.19\{HgSO_4(NH_3)_2\}15H_2O$; he regards L. Pesci's compound as a partially dehydrated slightly basic specimen of monohydrated mercuric diamminosulphate. Monohydrated mercuric diamminosulphate, $HgSO_4.2NH_3.H_2O$—*vide supra*—was regarded by

L. Pesci as an ammonium dimercuriammonium sulphate : $3(NH_4)_2SO_4.(NHg_2)_2SO_4.4H_2O$. The basic sulphate of Millon's base, $Hg(OH)_2.(NHg_2)SO_4(NH_4).(NHg_2)_2SO_4$, was prepared by C. F. Rammelsberg as a pale yellow powder by the action of a hot soln. of ammonium sulphate on freshly precipitated mercuric oxide.

A. F. de Fourcroy, and R. J. Kane treated mercuric sulphate with aq. ammonia, and found a yellow basic sulphate is first produced, and this is gradually transformed into a white powder. The reaction is the same if the liquid is boiling, but it then proceeds faster. This compound is the so-called *ammonia turpeth*. According to the analyses of R. J. Kane, N. A. E. Millon, C. H. Hirzel, and O. Schmieder, the composition corresponds with $Hg_4N_2H_4O_2.SO_4$, while P. C. Ray gave $Hg_4N_2H_2O.SO_4$, but without analyses. The constitution can be represented as an *oxydimercuriammonium sulphate*, $\{NH_2(HgOHg)\}_2SO_4$. E. C. Franklin regards it as a mixed hydroxy-amminio basic sulphate of mercury, and represents the analyses by $(HO.Hg.NH.Hg)_2SO_4$, or the *sulphate of Millon's base*, or **mercuric hydroxysulphatoamide.**

Ammonia turpeth is formed by the action of dil. sulphuric acid on Millon's base, $(HO.Hg)_2 : NH_2OH$, or on the hydroammonio base, $Hg : N.Hg.OH$. It is also made by the action of aqua ammonia on the basic sulphate $2HgO.Hg_2SO_4$; C. Ullgren prepared it by the action of a soln. of ammonium sulphate on the basic sulphate ; C. H. Hirzel, by the action of a soln. of ammonium sulphate on mercuric oxide ; N. A. E. Millon, by diluting with water a soln. of mercuric sulphate in conc. aq. ammonia ; and O. Schmieder, by the action of boiling water on hydrated mercuric diamminosulphate, $HgSO_4.2NH_3.H_2O$. C. Ullgren's and O. Schmieder's products had a yellowish tinge, while those of R. J. Kane, and C. H. Hirzel were white. The white powder obtained by N. A. E. Millon was crystalline, L. Playfair and J. P. Joule gave 7·319 for the sp. gr. at 3·9°. O. Schmieder said that it is not decomposed at 115° ; and R. J. Kane, that it turns brown when heated, giving off water, nitrogen, a trace of ammonia, and, according to O. Schmieder, and C. H. Hirzel, a little mercury, leaving behind mercurous sulphate. C. H. Hirzel also obtained some sulphur dioxide. According to C. Ullgren, and R. J. Kane, ammonia turpeth is sparingly soluble in water, and it is soluble in hydrochloric and nitric acids, giving off nitrous fumes—N_2O_3 ; the aq. soln. contains ammonia. C. H. Hirzel, and O. Schmieder found it to be insoluble in nitric acid ; and the former said that it is soluble in conc. sulphuric acid, forming ammonium mercuric sulphate, $(NH_4)_2SO_4.3HgSO_4.2H_2O$; O. Schmieder, however, said that it is insoluble in conc. sulphuric acid, but readily soluble in the dil. acid. C. H. Hirzel found that it is soluble in a soln. of ammonium sulphate, and, added O. Schmieder, without the evolution of ammonia ; O. Schmieder also found that it is soluble in a boiling soln. of ammonium chloride with the copious evolution of ammonia. R. J. Kane found that when hydrogen sulphide is passed into water with the powder in suspension, mercuric sulphide and a neutral soln. of ammonium sulphate are formed. C. Ullgren found no ammonia is evolved when it is treated with a soln. of potassium hydroxide ; but with a prolonged boiling, C. H. Hirzel obtained a little ammonia and a yellow product—O. Schmieder said yellow mercuric oxide is the ultimate product of this action. C. Ullgren obtained ammonia by treating the compound with potassium sulphide.

O. Schmieder obtained a product with the empirical composition $Hg_7N_4H_8O_3.2SO_4$, by the action of cold water on $HgSO_4.2NH_3.H_2O$, or by pouring a soln. of ammonium sulphate, sat. with mercuric oxide, into cold water. L. Pesci also made a compound with the same composition by a similar process, and also by the action of hot dil. nitric acid on his ammonium dimercuriammonium sulphate. This compound can be regarded as *mercuriammonium oxydimercuriammonium sulphate*, $(NH_2Hg)_2SO_4.3(NH_2HgOHg)_2SO_4$; or, according to L. Pesci, $(NH_4)_2SO_4.7(NHg_2)_2SO_4.12H_2O$, *i.e. dodecahydrated ammonium dimercuriammonium sulphate ;* or, according to E. C. Franklin, $(NH_2Hg)_2SO_4.3(HOHgNHHg)_2SO_4$, *i.e.* **mercuriammonium hydroxyamidosulphate.** L. Pesci found that a mol of the heavy white earthy powder loses three mols of water when heated to 115°, and furnishes

$Hg_7N_2H_4O_2.SO_4$, or, according to E. C. Franklin, $(NH_2Hg)_2SO_4.3(Hg_2N)_2SO_4$, *i.e.* **mercuriammonium dimercuriammonium sulphate.** O. Schmieder found that when heated in a closed tube, mercuriammonium hydroxyamidosulphate turns brown, gives off water, nitrogen, and mercury, and on cooling, white mercurous sulphate remains; when washed with boiling water, ammonium sulphate is extracted—according to L. Pesci, ammonia turpeth is formed. O. Schmieder found that a boiling dil. soln. of potassium hydroxide gradually converts it into mercuric oxide, and that a conc. soln. of ammonium sulphate converts it into $HgSO_4.2NH_3.H_2O$. A boiling soln. of ammonium chloride dissolves the salt completely with the evolution of ammonia. It is readily soluble in conc. and dil. hydrochloric acid, or in very dil. sulphuric acid, while it is not soluble in conc. sulphuric acid or in conc. or dil. nitric acid.

O. Schmieder prepared a product with the composition $Hg_5N_2H_4SO_4$, by dissolving $HgSO_4.2NH_3.2H_2O$ in dil. sulphuric acid; pouring the soln. into an excess of a dil. soln. of potassium hydroxide; and washing the precipitate with warm water. L. Pesci followed O. Schmieder's directions but failed to get this compound, and obtained instead ammonia turpeth. O. Schmieder regarded it as *oxydimercuriammonium oxytrimercuriammonium sulphate*, $\{NH_2(HgOHg)\}\{NH_2(HgOHgOHg)\}SO_4$; and E. C. Franklin regarded it as **mercuric hydroxyamido-oxysulphate,** $(HOHgNHg)_2SO_4.HgO$. O. Schmieder said that the white powder becomes yellowish-white at 115° without loss of weight, and when heated in a tube, it gives off water, mercury, and nitrous fumes; the reddish-brown sintered mass becomes white when cooled; if heated to a still higher temp. it melts, and bubbles with the evolution of sulphur dioxide; and if heated still more, all is volatilized. When boiled with a dil. soln. of potassium hydroxide, ammonia is evolved and the mass acquires a yellow colour; by the prolonged action of a conc. soln. of potassium hydroxide, the ultimate product is mercuric oxide; it is completely soluble in a boiling soln. of ammonium chloride with the evolution of ammonia; but it dissolves in a boiling soln. of ammonium sulphate without the evolution of ammonia. It is soluble in dil. and conc. hydrochloric acid, and in very dil. sulphuric acid; but insoluble in nitric acid and conc. sulphuric acid.

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§ 32. The Mercury Carbonates

In his essay *De acido aëreo* (Upsala, 1774), T. Bergmann obtained mercury carbonate by treating a soln. of mercury in an acid with an alkali carbonate. According to P. N. Raikow,[1] carbon dioxide has no action on mercurous oxide. H. Demarçay found that when a soln. of a mercurous salt is treated with potassium or sodium carbonate, a dirty white precipitate is formed; the corresponding hydrocarbonates give a white precipitate which becomes black when the liquid is boiled; and

ammonium carbonate gives a grey or black precipitate. According to C. Arnold, the precipitate produced by the addition of a soln. of alkali carbonate, ammonia, or potassium hydroxide to a mercurous salt soln. is not soluble in a sat. soln. of potassium carbonate, nor in a sat. soln. of ammonium carbonate in water or in 10 per cent. aq. ammonia. A. P. Castanares found that unlike bismuth salts, hot soln. of mercury salts, acidified with nitric acid, are not precipitated by ammonium carbonate. H. Rose obtained a reddish-brown oxychloride by adding alkali carbonate to a soln. of mercuric nitrate ; and K. Thümmel showed that when the alkali carbonate is added to a soln. of mercuric chloride, the oxychloride is precipitated, but if a soln. of mercuric chloride be added to one of the alkali carbonates, mercuric oxide is precipitated. D. Vitali, however, obtained no precipitation with a soln. of mercuric cyanide. If an ammonium salt be present, the alkali carbonates gives a white precipitate ; and if organic substances—sugar, gum, etc.—are present, a black precipitate is produced in a dil. soln. of a mercuric salt, and in conc. soln. a dirty yellow precipitate which becomes black in a few hours, or immediately on boiling.

According to R. Schindler, and E. Biltz, soln. of potassium or sodium hydrocarbonate give a reddish-brown precipitate when added to soln. of mercuric sulphate or nitrate ; and with an eq. amount of a soln. of mercuric chloride, a white turbidity appears which becomes reddish, and finally precipitates a reddish oxychloride—part of the mercury remains in soln. According to A. Barthélemy, the yellow precipitate produced by an alkali hydrocarbonate in a soln. of mercurous nitrate is soluble in an excess of the latter. H. Vittenet noted that natural waters containing hydrocarbonates in soln. give a precipitate with a 10 per cent. soln. of mercuric and ammonium chlorides. H. Demarçay found mercurous salt soln. are precipitated in the cold by magnesium carbonate, or by the alkaline earth carbonates, and H. Rose found that the precipitate is a mixture of mercuric oxide and the metal, not mercurous oxide, when barium carbonate is used, and that the precipitation is quantitative with mercuric sulphate or nitrate, but, even with boiling soln., mercuric chloride is not precipitated. E. Biltz thought that soln. in which there are 20 mols of sodium hydrocarbonate, or 45 mols of potassium hydrocarbonate, to one of mercuric chloride, contain a double salt of alkali hydrocarbonate and mercuric carbonate ; but K. Thümmel objected that mercuric carbonate is not produced from soln. of mercuric chloride—the mixed soln. gives off carbon dioxide.

More or less impure **mercurous carbonate,** Hg_2CO_3, is precipitated as a yellow powder when a soln. of mercurous nitrate is mixed with sodium or potassium carbonate ; and in order to get the salt quite sat. with carbon dioxide, J. Setterberg recommended mixing the nitrate with a slight excess of potassium hydrocarbonate and allowing the mixture to stand for a few days. The mixture is frequently agitated to ensure the decomposition of any basic mercuric nitrate which may have been precipitated. The precipitate is then quickly washed, and dried in vacuo over conc. sulphuric acid. H. Rose triturated crystalline mercurous nitrate with potassium hydrocarbonate and water, and washed the product as rapidly as possible. J. Lefort recommended dropping the mercurous nitrate soln. into a cold sat. soln. of potassium hydrocarbonate, washing with carbonic acid, and drying in darkness over sulphuric acid.

According to J. Lefort, the pale yellow powder does not amalgamate gold, showing the absence of free mercury—but if the powder has been exposed to light, the gold is quickly amalgamated. L. J. Proust found that the salt is converted into mercuric oxide and mercury when exposed to air ; some carbon dioxide is also given off. G. C. Wittstein stated that this decomposition readily occurs under warm water, and H. Rose that it is very rapid in boiling water. C. H. Pfaff added that if mercurous carbonate retains some alkali carbonate, employed as precipitant, the latter abstracts some carbon dioxide and the product turns black. J. Lefort found that the dried carbonate loses carbon dioxide at 130°, and forms mercuric oxide and mercury. G. C. Wittstein found that mercurous carbonate is blackened by aq.

ammonia, and some is dissolved with the separation of mercury ; the soln. deposits a white powder when exposed to the air, and on evaporation leaves a compound of ammonia and mercuric oxide. O. Hermes found a small trace of thiocyanic acid precipitates mercury.

According to P. N. Raikow, when carbon dioxide is passed into a mixture obtained by adding to a *N*-soln. of mercuric chloride, a quantity of potassium hydroxide sufficient to convert about one-fifth of the metal into hydroxide, the mercuric oxide is converted into normal **mercuric carbonate,** $HgCO_3$, mixed with a little acid carbonate. W. Leuze prepared **colloidal mercuric carbonate** by adding a dil. soln. of sodium carbonate to a dil. soln. of mercuric chloride and sodium protalbinate or lysalbinate. The soln. may be dialyzed.

N. A. E. Millon dropped a soln. of mercuric nitrate into a large excess of a soln. of potassium or sodium carbonate, and obtained an ochre-yellow powder, **mercuric trioxycarbonate,** $HgCO_3.3HgO$, or $4HgO.CO_2$. He also showed that if the alkali carbonate soln. be added to that of mercuric nitrate, as recommended by R. Phillips, the precipitate may be contaminated with some nitrate. The precipitate should be washed with cold water, and it can be dried at 130° without decomposition. Yellow mercuric oxide is formed when the product is treated with a soln. of potassium hydroxide. If potassium hydrocarbonate be employed as precipitant, N. A. E. Millon, and J. Setterberg obtained mercuric dioxycarbonate, $HgCO_3.2HgO$, or $3HgO.CO_2$. If a mixture of the mercuric salt and alkali hydrocarbonate be boiled, the precipitate contains scarcely a trace of carbon dioxide. According to K. Thümmel, when an alkali carbonate or hydrocarbonate is added to a soln. of mercuric nitrate, a white precipitate of basic nitrate, $2HgO.Hg(NO_3)_2$, is formed, and it is this, not the mercuric nitrate in soln., which forms $2HgO.HgCO_3$. According to G. C. Wittstein, and R. H. Brett, the brownish-red basic carbonate is slightly soluble in carbonic acid, or in a soln. of potassium carbonate, or ammonium chloride. W. C. Reynolds claimed to have made *potassium mercuric carbonate*, but " not crystalline or of definite composition " ; and A. Ferraro, an unstable *calcium mercuric carbonate* by adding mercuric chloride to calcareous waters free from ammonia.

C. F. Rammelsberg [2] boiled Millon's base with a soln. of sodium carbonate and dried the yellow product in a steam oven ; the analysis corresponded with $Hg_4N_2H_4O_2.CO_3$, and he represents it as *dimercuriammonium carbonate*, $(NHg_2)_2CO_3.2H_2O$, while E. C. Franklin represents it as **mercuric hydroxyamidocarbonate,** $(HOHgNHHg)_2CO_3$. L. Pesci stated that it reacts vigorously with a soln. of ammonium bromide. N. A. E. Millon passed carbon dioxide through water in which Millon's base was suspended, or treated Millon's base with a soln. of ammonium carbonate or potassium hydrocarbonate, and obtained what he regarded as oxydimercuriammonium carbonate, $\{NH_2(HgOHg)\}_2CO_3.\frac{1}{2}H_2O$, but E. C. Franklin regarded it as a hemihydrate, $(HOHgNHHg)_2CO_3.\frac{1}{2}H_2O$. C. H. Hirzel obtained the same product by boiling a soln. of ammonium carbonate in contact with mercuric oxide ; F. Seemann preferred an ammoniacal soln. of ammonium carbonate. According to C. H. Hirzel, the product is a yellow powder which gradually becomes grey on exposure to light. The dried carbonate does not lose water at 130°, but at 145°, 1·01 to 1·80 per cent. of water is given off, and at 180°–200° more water and ammonia are evolved. F. Seemann found that a litre of water dissolves 0·003 grm. of the salt. It is decomposed by conc. hydrochloric acid, forming NH_2HgCl ; with a boiling soln. of potassium hydroxide no ammonia is given off ; with a soln. of potassium iodide or sulphide, the whole of the nitrogen is given off as ammonia ; conc. nitric acid reacts vigorously, forming nitrates ; sulphuric acid has scarcely any action in the cold, but when boiling, sulphates are gradually formed ; and with a soln. of sodium silicate, the silica is all precipitated. C. H. Hirzel digested mercuric oxide with a cold soln. of ammonium carbonate, and obtained a monohydrated form of this carbonate as a snow-white powder which turns grey in light and reacts like the hemihydrate. These three compounds, said E. C. Franklin, " cannot be essentially different."

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§ 33. Arrested Reactions

There are a number of reactions which give different products according to the mode of mixing the reacting constituents. Thus, C. F. Gerhardt [1] found that if a neutral soln. of lead nitrate be added to a soln. of sodium phosphate in excess, a flocculent precipitate of normal lead phosphate, $Pb_3(PO_4)_2$, is obtained: on the other hand, if the sodium phosphate soln. be added to the lead nitrate soln. in excess, monoclinic crystals of a lead nitratophosphate, say, $Pb_2(NO_3)PO_4$, are obtained. The former precipitate becomes anhydrous at 100°, the latter requires a much higher temp. to drive off the water. With copper sulphate and potassium hydroxide a green basic copper sulphate, $n\mathrm{Cu(OH)_2}.m\mathrm{CuSO_4}$, is precipitated when the latter is added to an excess of the former; and blue copper hydroxide, $Cu(OH)_2$, when the admixture is made in the inverse manner. K. Thümmel noted that alkali carbonate soln. added to mercuric chloride soln. gives mercuric oxychloride, while if the soln. be mixed in the reverse order, mercuric oxide is precipitated; J. Messner, that when potassium ferrocyanide is poured into an excess of a soln. of copper sulphate, the precipitated potassium copper ferrocyanide has less potassium than if the soln. be mixed in the reverse order; F. Raschig, that the colour reaction between aniline and sodium hypochlorite is or is not obtained according as ammonia is added before or after the two soln. are mixed; and J. Sperber, that when hydriodic acid is added to hydrogen peroxide, a colourless liquid is obtained, but when the mixing is done in the reverse order, there is a separation of iodine. In analytical work, also, the composition of the precipitate may depend on the way the soln. are mixed; thus G. A. Hulett and L. H. Duschak, and G. McP. Smith found this to be the case with barium sulphate precipitated from acid soln. of barium chloride; and E. G. Beckett, with antimony sulphide precipitated from acid soln. of antimony chloride.

The phase rule would say that equilibrium is not attained in these reactions, and that the state of equilibrium is attained more nearly by one method of mixing than in another; and that once a precipitate has been formed the time required for the subsequent progress of the reaction may be so slow that the composition of the precipitates appear permanently different. The phase rule, however, assumes that an indefinitely long time is available. The observed fact is that the products of some reactions are determined by the mode of mixing. C. L. Berthollet said:

> The faculty of combining more quickly with one substance than with another sometimes produces precipitations which may be considered as accidental, and which do not take place if the circumstances render the action slower. T. Bergman observed that when conc. sulphuric acid was poured into a sat. soln. of potassium sulphate, alum, ferrous sulphate, mercuric chloride, or other salts which water dissolves with difficulty, the salts were

rapidly precipitated; but if the sulphuric acid was poured in by small portions and the liquid agitated, these precipitations did not take place. The same phenomenon is observed on suddenly mixing an aq. soln. of barium chloride with conc. hydrochloric acid, and in a great number of other circumstances in which it is seen that a precipitate is formed at the first instant of the mixture, and afterwards redissolved slowly or more quickly by the assistance of heat or of agitation.

If the reaction be arrested while in progress, the mode of mixing is of vital importance in order to obtain particular products, because the final state of equilibrium may be attained by different paths by the different modes of mixing. This is still more the case in reactions between mixtures of powdered solids. Even with liquids it is by no means easy to get a homogeneous mixture in a short time by agitation. Thus, C. L. Berthollet said:

> Although sulphuric acid exercises a brisk action on water and retains it strongly, nevertheless, it is difficult to bring it to a uniform soln. so that when the liquor is interposed between the eye and the light it shall not appear striated. It is the same with alcohol.

Similarly with molten glass for optical purposes, in spite of the fact that the molten glass is stirred for many hours, it is very difficult to manufacture large pieces free from striæ. There are numerous industries—*e.g.* cement, lime, plaster of Paris, annealed metals, pottery (*q.v.*), etc.—in which success or failure depends on the arresting of reactions at precisely the right stage; and this, in turn, often depends on differences in the modes of mixing; and on differences in the nature of the components employed to furnish a product with the same ultimate composition.

According to F. Auerbach and H. Pick, even the state of equilibrium of the reaction between lead chromate and sodium carbonate is determined by the mode of mixing the reacting constituents. They showed that the state of equilibrium: $2PbCrO_4+2Na_2CO_3+H_2O \rightleftharpoons PbO.PbCrO_4+2NaHCO_3+Na_2CrO_4$, is not the same when the start is made from different sides; although it is not unlikely that if an indefinitely long time were available, the same end-state would be attained. A precipitate may have more time to change into a polymeric, less reactive form when obtained by one process than by another process, and this secondary reaction might make it appear that the products are different when obtained in different ways. The reaction $PbCO_3 \rightleftharpoons PbO+CO_2$, is not reversible like the corresponding reaction $CaCO_3 \rightleftharpoons CaO+CO_2$, because the lead oxide immediately changes into a less reactive form; if water vapour be present, the lead oxide does not change so rapidly and the reaction is then reversible. Again, P. P. von Weimarn showed that the physical character of precipitates is largely determined by the conditions under which the precipitating salts interact; F. J. Otto, that precipitated gold is finer when obtained by pouring ferrous chloride into a soln. of gold chloride, than when the latter is poured into the former; and J. L. Gay Lussac, that the tint of purple of Cassius is determined by the rapidity of admixture.

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§ 34. Mercurous Nitrate

Mercury nitrate was known to the mediæval alchemists. It is mentioned by A. Libavius,[1] Basil Valentine, etc. T. Bergman distinguished the variety prepared with cold nitric acid from that prepared with hot nitric acid, and this was

later shown to depend on the existence of higher and lower states of oxidation, the former corresponding with mercuric nitrate, $Hg(NO_3)_2$, where mercury is bivalent, and the latter with mercurous nitrate, $HgNO_3$, where mercury is univalent —*vide supra*. There are also several basic nitrates. In 1806, A. F. de Fourcroy and L. J. Thénard said that black and red mercury oxides each *se combinerait en trois proportions différentes à l'acide azotique.*

Short prismatic crystals of **mercurous nitrate,** $HgNO_3$, were obtained by C. G. Mitscherlich [2] by leaving cold dil. nitric acid upon an excess of mercury. According to W. Reuss, in the action of cold dil. nitric acid on mercury, only the normal salt is produced whether the acid or the mercury is in excess, for these only affect the water of crystallization of the resulting salt. A low temp. and dil. acid favour the formation of crystals with a large proportion of water of crystallization. If the mercury and acid be heated on the water-bath, the normal salt is alone produced. The effects of an excess of the acid or mercury are the same provided that the proportion of free acid does not fall below 4–5 per cent. nor rise above 15–20 per cent. If the conc. of the free acid be smaller than 4–5 per cent., a basic salt will be formed, and if higher than 15–20 per cent., a mercuric salt will be produced. If the crystals are left in the soln. for a long time, C. G. Mitscherlich, and J. A. W. Büchner observed that crystals of a basic nitrate are formed. This reaction no doubt depends on the conc. of the free acid in the soln. P. C. Ray recommended using an acid with a sp. gr. between 1·135 and 1·140 ; J. Lefort, nitric acid of sp. gr. 1·42 diluted with 1–2 times its vol. of water ; and J. C. G. de Marignac, nitric acid diluted with 2–3 times its vol. of water. N. A. E. Millon, W. J. Russell, and V. H. Veley regard mercurous nitrate as a secondary product of the action of nitric acid on mercury ; E. Divers, as a primary product—*vide* action of nitric acid on mercury. C. F. Bucholz dissolved mercury in moderately conc. nitric acid, evaporated the soln. to dryness, triturated the residue with mercury and water in a hot mortar until the fluidity of the metal is destroyed, dissolved the mass in hot water slightly acidulated with nitric acid, filtered, and cooled the liquid for crystallization. P. C. Ray noted that mercuric nitrate is formed by the action of dil. nitric acid on mercurous nitrite ; and J. Lefort, and W. Reuss, by the action of dil. nitric acid on the basic salts of mercury. C. Barfoed noted that a soln. of mercuric nitrate dissolves finely divided mercury, and P. C. Ray showed that when a soln. of mercuric nitrate is violently shaken for a short time with mercury, it is wholly converted into mercurous nitrate, and he recommended this method of preparing a soln. of mercurous nitrate free from nitrous acid. A. Ogg also recommended preparing a neutral soln. of mercurous nitrate by shaking a soln. of mercuric nitrate with mercury, and filtering the soln. from the solid basic nitrate. Analyses of the crystals by C. G. Mitscherlich, C. F. Gerhardt, J. C. G. de Marignac, A. J. Cox, etc., show that monohydrated mercurous nitrate, $HgNO_3.H_2O$, is in question. J. Lefort's analyses corresponded with the hydrate $Hg_2(NO_3)_2.2\frac{3}{4}H_2O$, but J. C. G. de Marignac showed that the crystals were probably not dry, for they are liable to contain inclusions of the mother liquor ; the crystals should be powdered and dried by press. between folds of filter paper. W. Reuss claimed to have produced a whole range of other hydrates with $1\frac{1}{4}$, $1\frac{1}{3}$, $1\frac{1}{2}$, $1\frac{2}{3}$, 2, $2\frac{1}{5}$, $2\frac{1}{4}$, $2\frac{1}{2}$, 3, and $3\frac{1}{2}H_2O$, but this has not been confirmed.

The prismatic **crystals** of the monohydrate were found by J. C. G. de Marignac to belong to the monoclinic system, and to have axial ratios $a:b:c=1·1503:1:0·8334$, and $\beta=103°\ 47\frac{1}{2}'$. The salt does not crystallize isomorphously with the other univalent nitrates. Mercurous nitrate is very hygroscopic. L. Playfair and J. P. Joule [3] found the **specific gravity** of the monohydrate to be 4·785 at 3·9°. C. F. Gerhardt found that the crystals of the monohydrate melt readily when heated ; J. Lefort gave 70° for the **melting point.** According to J. Lefort, the monohydrate slowly loses all its water when exposed to the air, and rapidly in vacuo over sulphuric acid. The crystals of the hydrate effloresce slightly in air. The salt decomposes into nitrogen peroxide and mercuric oxide when heated to a higher temp. F. Canzoneri found from the lowering of the **freezing point of solutions** in dil.

nitric acid a value corresponding with the mol. wt. $Hg_2(NO_3)_2$, and not $HgNO_3$; but A. Ogg showed that too much confidence should not be placed on this result because of the ionization of the solute. With the anhydrous salt, P. W. Bridgman could detect no signs of a transition into another form at temp. between 20° and 90°, and at higher temp. the salt decomposes. The monohydrate probably has a transition at 20° and 8000 kgrms. per sq. cm. press. R. Varet gave for the **heat of formation,** $2Hg_{liq.}+N_2+3O_2+2H_2O_{liq.}=2Hg_2(NO_3)_2.2H_2O_{solid}+69{\cdot}4$ Cals.; and J. Thomsen gave (2Hg, O, $2HNO_{3aq.}$)=47·99 Cals.; and (Hg_2O, $2HNO_{3aq.}$)=5·79 Cals. R. Varet gave for the **heat of solution** of $Hg_2(NO_3)_2.2H_2O$ in dil. nitric acid, −12·4 Cals. P. T. Muller and E. Carrière found the mean **specific refraction** of soln. of mercurous nitrate in 0·6*N*- to 1·05*N*-HNO_3 in yellow light, to be 0·0843, *i.e.* about 7·8 per cent. greater than that of mercuric nitrate; the **specific dispersion** is about 10·5 per cent. greater, being 0·0063. C. Schaefer and M. Schubert investigated the **infra-red spectrum** of mercury nitrate. A. Ogg found the mol. conductivity, λ, of soln. of mercurous nitrate in $\frac{1}{10}N$-HNO_3 increases 34 per cent. when v, the number of litres of soln. per mol. of salt, changes from 5 to 250. At 18°:

v	5	9	16	32	70	130	225
$\lambda\times10^7$	51·85	53·72	54·87	55·50	62·25	64·80	69·58

W. Reinders found that mercurous nitrate is not so strongly ionized as silver nitrate in aq. soln. A. Ogg also found that the **decomposition voltages** of soln. of mercurous nitrate are nearly the same as those of soln. of silver nitrate. E. Bouty has measured the **electromotive force** of soln. of mercurous nitrate. R. Behrend measured the e.m.f. of soln. in various organic solvents; and E. Baur, the e.m.f. between a soln. of mercurous nitrate and various organic liquids.

J. von Tugolessoff [4] argued that the **action of light** always tends to an oxidizing reaction, and cited, *inter alia,* the following:

> Ordinary writing paper was soaked in a sat. soln. of mercurous nitrate, dried, and exposed to light. My idea was that, if the action of light were an oxidizing one, an insoluble basic mercuric salt would form where the paper was illuminated and would remain on the paper after the unchanged mercurous nitrate has been washed out. The action of light produced no visible change in the paper; but when the paper had been washed in boiling water, the exposed places assumed a yellowish colour which then changed to a dark grey, making the image fairly distinct. The theory was confirmed. Under the action of light there was formed a colourless, insoluble mercuric salt which was changed by a large excess of water into a yellow salt, $Hg(NO_3)_2.2HgO.H_2O$. This latter reacted with the excess of mercurous nitrate in the soln., forming mercuric nitrate and mercurous oxide. The mercurous oxide was decomposed by boiling water into oxygen and metallic mercury.

S. Hada found that mercurous nitrate is stable in **air** if not exposed to a bright light. A. Colson found that at 100°, in presence of **hydrogen,** the dried crystals become yellow and give off nitric oxide; and at 100°, they absorb **oxygen,** and form mercuric nitrate; and J. L. Proust said that a soln. of mercurous nitrate exposed to the air, absorbs oxygen, forming mercuric nitrate. A. Mailfert said that **ozone** transforms mercurous nitrate into mercuric nitrate and a basic mercuric nitrate, and Y. Yamauchi that aq. soln. of mercurous nitrate are oxidized by ozone to mercuric oxide and nitrate. According to S. Hada, an aq. soln. in darkness and in a closed vessel is quite stable when it is free from nitrous acid, and this even in an atm. of oxygen; there is no evidence that any mercurous salt, moist or in soln., is oxidizable in air at ordinary or moderate temp. The experiments of L. Mailhe on the oxidizability of wet mercurous chloride in air really show that it is the mercurous oxide which is oxidized, for the mercurous salt is decomposed under these conditions into a basic salt. Mercurous salts in the presence of water, or better, in soln., are oxidized in air or oxygen at about 150°. In strong light, mercurous nitrate, moist or in soln., is dissociated at common temp., forming the mercuric salt and mercury—the change is produced by the reduction of its own nitric acid to nitrous acid. Exposure in an open vessel, or to an atm. of mercury vapour or even to oxygen, retards the progress of the change, by keeping down the quantity of nitrous acid which otherwise increases with time. An atm. of carbon dioxide does not impede the change.

Mercurous nitrate is readily changed to mercuric nitrate and nitrite when kept in soln. at 150° under press. J. L. Proust knew that on boiling a soln. of mercurous nitrate, mercury is volatilized with the steam; H. Rose also stated that when mercurous nitrate is continuously boiled with water, it is converted into mercuric nitrate and mercury, but he wrongly thought that the insoluble salt formed when mercurous nitrate is treated with water, contained both mercury and mercuric nitrate. The dissociation of mercurous nitrate noted by J. L. Proust was shown by S. Hada to proceed at lower temp., even to a measurable extent at 40°, provided that the mercury vapour is carried away by a current of air.

According to J. L. Proust, and P. Grouvelle, mercurous nitrate dissolves completely in a small proportion of warm **water,** but with a larger proportion of water, the salt is hydrolyzed, forming an acid soln. and an insoluble basic salt, which contains less nitrate and more oxide the greater the proportion of water, until finally A. J. Cox found mercuric oxide alone remained. Mercurous nitrate is completely soluble in water acidified with nitric acid; and A. J. Cox found that at least 2·95 N-HNO_3 is necessary at 25° to maintain the mercurous nitrate in soln. The soln. of mercury in cold dil. nitric acid or of mercurous nitrate in dil. nitric acid is the *solutio mercurii frigide parata*—soln. of mercury prepared in the cold. A. Libavius, and J. L. Proust mentioned that if the skin be wetted with this soln. and exposed to light, a purple stain appears which finally becomes black.

When a soln. of mercurous nitrate is treated with **chlorine,** H. Hager found that mercurous chloride, and mercuric nitrate are formed; and R. Varet, that the nitric acid of mercurous nitrate is displaced by **hydrogen chloride,** C. G. Mitscherlich found that when mercurous nitrate is triturated with **sodium chloride,** and the mixture extracted with water, the filtrate contains neither free acid nor mercury; insoluble mercurous chloride and sodium nitrate are formed. J. Myers found mercurous nitrate is reduced to mercury by **potassium hydrosulphide.** L. V. Brugnatelli found that when projected on red-hot **carbon,** mercurous nitrate detonates feebly but with a bright flame. C. W. Scheele observed that when mercurous nitrate is treated with **hydrocyanic acid,** metallic mercury appears; F. John said that mercuric cyanide is simultaneously formed, and M. H. Deschamps that soluble mercuric cyanide, ammonium nitrate, and carbonate are formed. R. Varet found that the nitric acid is displaced from mercurous nitrate by hydrogen cyanide. G. C. Wittstein obtained a white gelatinous precipitate with **potassium ferrocyanide,** and a brown precipitate with **potassium ferricyanide;** H. Arctowsky noted that mercurous nitrate dissolves appreciably in boiling **carbon disulphide.** A. Naumann said that mercurous nitrate is slightly soluble in **benzonitrile;** and H. D. Gibbs that liquid **methylamine** colours the salt black and dissolves it. L. Pesci found that when mercurous nitrate is treated with **ammonia** gas, mercury is formed. E. C. Franklin and C. A. Kraus found that the salt is insoluble in liquid ammonia; and H. Hager, that a glass rod moistened with a soln. of mercurous nitrate held in ammonia vapour, forms a white film which later becomes black. A. F. de Fourcroy noted that aq. ammonia gives a grey precipitate with mercurous nitrate. W. Reuss obtained white crystals of what he regarded as octohydrated **mercurous hydropentanitrate,** $4HgNO_3.HNO_3.8H_2O$, by evaporating the mother liquid remaining after the separation of the basic 16 : 9 : 19 salt; and yellow crystals of the acid salt $5HgNO_3.3HNO_3,26H_2O$ from the mother liquid remaining after the separation of the basic 8 : 5 : 11 salt. L. V. Brugnatelli found that a mixture of **phosphorus** and mercurous nitrate detonates violently when struck with a hot hammer. H. Rose obtained a black precipitate by passing **phosphine** into a soln. of mercurous nitrate. G. Denigès used mercurous nitrate as a micro-chemical test for **arsenic;** and H. Rosenhaupt used it for producing bronze effects on metals. According to A. Ogg, finely-divided **silver** precipitates mercury from a soln. of mercurous nitrate, and this amalgamates with the silver.

S. Hahnemann [5] described a product formed by the action of a cold very dil. soln. of mercurous nitrate, as free as possible from an excess of nitric acid and of mercuric nitrate,

on less than an eq. quantity of a dil. aq. or alcoholic soln. of ammonia added very gradually with constant stirring. The precipitate is quickly washed on a filter by means of cold water, pressed between filter paper, and dried in darkness at ordinary temp. Special directions have been given for preparing this compound in many pharmacopœias, and likewise by C. G. Mitscherlich, C. F. Bucholz, F. W. Beissenhirtz, R. Brandes, G. Stein and J. A. W. Büchner, J. S. F. Pagenstecher, G. H. Stolze, A. M. Pleischl, A. Duflos, A. Monheim, etc. The black or greyish-black powder has been called *mercurius solubilis Hahnemanni*, or *Hahnemann's soluble mercury*. According to A. Duflos, when Hahnemann's mercury is exposed to light, it is gradually decomposed into mercury and a basic mercuric nitrate; and when heated in a glass tube it sublimes without residue—the sublimate is mercury; but J. A. W. Büchner said the sublimate is a basic mercuric nitrate. With a soln. of potassium hydroxide, C. G. Mitscherlich obtained a little ammonia, E. Soubeiran obtained none. C. G. Mitscherlich said that baryta water removes part of the acid radicle, while a soln. of barium sulphide takes away all the acid, and drives off ammonia. E. Soubeiran found that with sulphuric acid, nitrous fumes are evolved. C. G. Mitscherlich found boiling hydrochloric acid dissolves Hahnemann's mercury completely, forming a soln. of mercuric and ammonium chlorides; cold hydrochloric acid forms mercurous chloride and dissolves out some mercuric oxide possibly present as an impurity—sometimes a detonating compound is formed with cold hydrochloric acid. According to C. F. Bucholz, cold dil. nitric acid dissolves mercurous oxide or, according to E. Soubeiran, basic mercurous nitrate, and leaves a less soluble white salt which C. F. Bucholz regarded as basic mercurous ammonium nitrate, and E. Soubeiran, as basic mercuric ammonium nitrate. C. F. Bucholz found boiling acetic acid dissolves all Hahnemann's mercury with the exception of a few globules of elemental mercury. C. G. Mitscherlich found it to be resolved by aq. ammonia into mercury and a soluble basic mercuric ammonium nitrate; and G. C. Wittstein found it behaved similarly with soln. of ammonium chloride, sulphate, or nitrate—particularly if heated. According to J. Lefort, Hahnemann's soluble mercury does not yield any globules of mercury when pressed, nor does it amalgamate gold foil. L. Pesci regarded Hahnemann's soluble mercury as a mixture of mercury with $3(NHg_2)NO_3.NH_4NO_3.2H_2O$, and he represented the reaction: $12HgNO_3+12NH_3+2H_2O=3NHg_2NO_3.NH_4NO_3.2H_2O+6Hg+8NH_4NO_3$. Analyses have been made by J. Lefort, C. G. Mitscherlich and A. Duflos, and these correspond with $3Hg_2O.N_2O_5.2NH_3.H_2O$; A. Lösch gave $(NH_2)_2Hg_2.Hg_2(NO_3)_2$; R. J. Kane gave $2Hg_2O.N_2O_5.2NH_3$, and it may possibly be a **mercurous ammino-nitrate**, but E. Soubeiran regarded it as a variable mixture of basic mercurous nitrate, and a salt to which he gave the name *protonitrate ammoniaco-mercuriel*, and which has also been called *Soubeiran's mercurous salt*. The latter was obtained by mixing a soln. of mercurous nitrate with a large proportion of nitric acid, or ammonium nitrate, and precipitating by adding ammonia; or by adding ammonia to a soln. of mercurous nitrate until the precipitate begins to whiten; the filtrate is then precipitated by ammonia. J. S. F. Pagenstecher, C. G. Mitscherlich, R. J. Kane, and E. Soubeiran were unable to agree as to whether this product is a mercurous or mercuric salt. It is now considered to be the nitrate of Millon's base (*q.v.*) mixed with a little mercury. Another old medicinal preparation, called *mercurius cinereus Blackii* or *mercurius cinereus Edinburgensium*, was obtained by precipitating mercurous nitrate with ammonium carbonate. The product is almost identical with Hahnemann's soluble mercury, but gives off a small quantity of carbon dioxide when treated with acids.

J. S. F. Pagenstecher[6] prepared columnar crystals of **ammonium mercurous nitrate,** $2NH_4NO_3.HgNO_3$, or $(NH_4)_2Hg(NO_3)_2$, by evaporating a mixed soln. of ammonium and mercurous nitrates. C. F. Rammelsberg found the rhombic bipyramids have axial ratios $a:b:c=0{\cdot}6924:1:0{\cdot}3649$. The aq. soln. gives a grey precipitate with an aq. soln. of ammonia, or potassium carbonate; the precipitate is a mixture of mercury and $NH_2HgNO_3.NH_2(HgOHg)NO_3$. The same salt was probably obtained by J. A. W. Büchner in the preparation of Hahnemann's mercury, but he regarded it as a basic mercurous nitrate.

The basic mercurous nitrates.—The hydrolysis of normal mercurous nitrate by water results in the formation of a basic salt and an acidic soln. The various reports of this action are confused. The basicity of the product is dependent on the quantity of water, on the temp., and on the time the reacting components are in contact. W. Reuss[7] stated that the water of crystallization is directly proportional to the number of salt-forming atoms of mercury in the product; that most of the basic salts crystallize in the rhombic system, a few in the monoclinic system; that the basic salts resist chemical and physical influences better than the normal salt; that unlike the normal salt, the basic salts do not smell of nitric acid; and that the water of crystallization usually remains when the salt is exposed to the air or kept in vacuo. A. J. Cox added that the mercuric salts are more susceptible to hydrolysis than the mercurous salts.

According to A. J. Cox, the mercurous nitrates which can be formed in aq. soln. are the monohydrate, $HgNO_3.H_2O$, in colourless crystals; white pulverulent $5Hg_2O.3N_2O_5.2H_2O$; a dirty-white product between $3Hg_2O.N_2O_5$ and $2Hg_2O.N_2O_5$, but whose existence is uncertain since it has not been isolated, though it appears to be formed by the hydrolysis of mercurous nitrate at 12°; a product darker than the preceding, $2Hg_2O.N_2O_5$; yellowish-green $3Hg_2O.N_2O_5.2H_2O$, whose existence is certain but whose composition is not definitely known. The results are shown graphically in Fig. 39, where the ordinates represent the number of mols of $(H, Hg)NO_3$ per litre of soln., and the abscissæ, the increased basicity x of the solid phase $10HgNO_3 - xN_2O_5$. The greenish-yellow basic salt, $3Hg_2O.N_2O_5.2H_2O$, or $2Hg_2O.2HgNO_3.2H_2O$, or $2HgOH.HgNO_3$, **monohydrated mercurous dioxynitrate,** was prepared by A. J. Cox by the hydrolysis of mercurous nitrate at 25°; an acid conc. of at least $0{\cdot}0017N$-HNO_3 is necessary. The salt decomposes at 90°. A. J. Cox found an acid conc. of at least $0{\cdot}110N$-HNO_3 at 25° to be necessary for the formation of **mercurous oxydinitrate,** $Hg_2O.2HgNO_3$; but the compound was not isolated—*vide* Fig. 39.

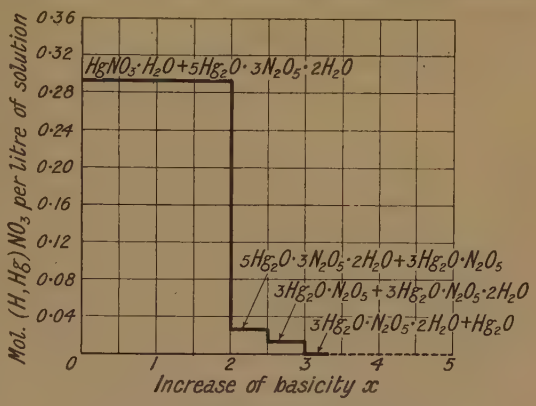

Fig. 39.—Basic Mercurous Nitrates.

C. F. Gerhardt's *sous-nitrate sesquimercureux* had the composition $3Hg_2O.2N_2O_5.H_2O$, or $Hg_2O.4HgNO_3.H_2O$, or $HgOH.2HgNO_3$, **mercurous hydroxydinitrate.** C. G. Mitscherlich prepared colourless prismatic crystals of this salt by leaving mercurous nitrate in the acid mother liquid in which it was prepared until the crystals have dissolved and been replaced by the crystals of the new salt; and by heating mercurous oxide with dil. nitric acid. C. G. Mitscherlich found the crystals obtained by these two processes are different, and hence stated that the salt is dimorphous; but C. F. Gerhardt showed that this is a mistake because the second process furnishes crystals of $5Hg_2O.3N_2O_5.2H_2O$. The salt was also made by J. C. G. de Marignac, C. F. Gerhardt, J. Lefort, and L. Mailhe. While C. G. Mitscherlich's analysis corresponds with the ratio $Hg_2O : N_2O_5 : H_2O = 3 : 2 : 3$, that of C. F. Gerhardt's corresponds with $3 : 2 : 1$; that of J. Lefort, with $3 : 2 : 2\frac{1}{2}$; and that of J. C. G. de Marignac's with $4 : 3 : 1$—*vide infra.* R. J. Kane believed the salt to be a mixture of normal mercurous nitrate with the $2 : 1 : 1$ salt.

R. J. Kane prepared **monohydrated mercurous oxydinitrate,** $Hg_2O.2HgNO_3.H_2O$, *i.e.* **mercurous hydroxynitrate,** $HOHg.HgNO_3$, also called *nitrous turpeth.* C. F. Gerhardt called it *sous-nitrate bimercureux;* and J. Lefort's analysis corresponded with $2Hg_2O.N_2O_5.2H_2O$, but his preparation was probably not well enough dried. This basic salt is obtained by washing basic or normal mercurous nitrate with cold water until it has acquired a yellow colour. The hydrolysis is more quickly produced by boiling water, but the action must be stopped as soon as a grey coloration appears owing to the separation of mercury; the reaction is also hastened by a little potassium hydroxide, but the product is then more impure. The grey powder obtained by M. Donovan by treating this salt with a soln. of potassium hydroxide is not a basic salt, but a mixture of the yellow salt with mercurous oxide. R. J. Kane also prepared the yellow salt in needle-like crystals when a soln. of mercurous nitrate is allowed to stand a long time over mercury. According to J. C. G. de Marignac, one part of powdered mercurous nitrate is agitated with ten parts of boiling water; and the yellow powder is washed by decantation with cold water. It should be dried in darkness. P. C. Ray obtained this salt from mercurous nitrite which he found to change into mercuric nitrite, which is

readily hydrolyzed, forming mercuric hydroxynitrate which reacts with mercurous nitrate, forming mercurous hydroxynitrite : $2Hg_2(NO_3)_2+3Hg+Hg(NO_2)_2+2H_2O=2NO+4(HOHg.HgNO_3)$. When this salt is heated, it gives off red vapours containing some nitric acid, and mercuric oxide remains. R. J. Kane, and J. C. G. de Marignac noted that it is gradually blackened when boiled with water ; the water afterwards contains some mercuric nitrate.

J. C. G. de Marignac prepared $5Hg_2O.3N_2O_5.2H_2O$, or $4(HOHg.HgNO_3).2HgNO_3$, or $2HgOH.3HgNO_3$, **mercurous dihydroxytrinitrate,** by boiling for many hours with mercury the soln. or the mother liquid remaining after the preparation of mercurous nitrate or of the basic nitrate, $4Hg_2O.3N_2O_5.H_2O$, replacing the water as it evaporates ; and also by leaving the two last-named salts in contact with their mother liquids and mercury at ordinary temp. C. F. Gerhardt made it by suspending mercurous nitrate in a little water which was heated to the b.p. and allowed to cool ; L.Pesci, by allowing a soln. of mercurous nitrate with the smallest possible quantity of nitric acid to stand in an atm. containing some ammonia gas ; J. Lefort, by evaporating to dryness the soln. obtained by the action of conc. nitric acid on mercury, and extracting the product with boiling water ; by mixing a soln. of mercurous nitrate with potassium hydrocarbonate until a precipitate is produced, and allowing the clear liquid to crystallize by evaporation ; and also by heating dil. nitric acid to 40°–80° in contact with mercury for a long time ; A. J. Cox, by the hydrolysis of a soln. of mercurous nitrate at 25°, Fig. 39, and he showed that an acid conc. of at least 0·293*N*-HNO_3 is necessary for its existence in soln. ; and P. C. Ray, by the slow action of dil. nitric acid on mercurous nitrite, and by the hydrolysis of a soln. of mercurous nitrite. There has been a controversy as to the exact composition of this salt ; J. C. G. de Marignac gave the ratio $Hg_2O : N_2O_5 : H_2O$ as 5 : 3 : 2. C. F. Gerhardt gave 2 : 1 : 1, and J. Lefort gave 2 : 1 : 2. The analyses of P. C. Ray, and A. J. Cox agree with those of J. C. G. de Marignac. The clear, colourless, prismatic crystals are triclinic pinacoids with axial ratios and angles, according to J. C. G. de Marignac, and C. F. Rammelsberg, of $a : b : c=1·3061 : 1 : 1·1904$, and $\alpha=94°\ 2'$, $\beta=109°\ 40'$, and $\gamma=101°\ 16'$. According to P. C. Ray, the crystals retain their lustre when exposed to air, or when confined over conc. sulphuric acid in vacuo. If heated for about 3 hrs. the crystals lose their water and form $5Hg_2O.3N_2O_5$; and they decompose when rapidly heated to 90° in an air-bath. W. Reuss also reported the hydrates 5 : 3 : 2 ; 5 : 3 : 4 ; and 5 : 3 : 6.

J. C. G. de Marignac obtained the 4 : 3 : 1 salt, or $3HgNO_3.HgOH$, **mercurous hydroxytrinitrate,** by heating crystals of mercurous nitrate with the mother liquid from which they separated, and an excess of mercury ; and cooling the soln. J. Lefort boiled mercury with nitric acid of sp. gr. 1·42 diluted with 5 vols. of water for 5 or 6 hrs. and replaced the water as it evaporates. If the mixture is not boiled long enough, the 5 : 3 : 2 salt is produced. P. C. Ray prepared the salt by digesting 50 grms. of mercury and 75 grms. of nitric acid of sp. gr. 1·2, first cold, and then warm ; the crop of crystals of mercurosomercuric nitrate which separates from the hot soln. is removed, and the 4 : 3 : 1 salt crystallizes out on cooling. P. C. Ray obtained the same salt by the hydrolysis of mercurous nitrate. The crystals form colourless needles or prisms which, according to J. C. G. de Marignac, are rhombic bipyramids with axial ratios $a : b : c=1·1132 : 1 : 0·9255$. The crystals do not change in air or in vacuo ; but at 100° they become yellow, and lose water. J. Lefort gave the formula 6 : 4 : 3, and there is some confusion in literature between this and the 3 : 2 : 1 salt. W. Reuss also described the hydrate 4 : 3 : 5, and reported products 8 : 5 : 5 ; and 8 : 5 : 11.

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§ 35. Mercuric Nitrate

A soln. of **mercuric nitrate,** $Hg(NO_3)_2$, the so-called *solutio mercurii calide parata*—soln. of mercury prepared by heat—of the older chemists, is readily obtained by dissolving mercuric oxide in nitric acid; and by boiling mercury or mercurous nitrate with an excess of nitric acid until a drop diluted with water

no longer becomes turbid when treated with a soln. of sodium chloride. For a long time it was supposed that the soln. of mercuric nitrate was uncrystallizable; J. L. Proust obtained a syrupy liquid of sp. gr. 3·47, but both J. L. Proust, J. A. W. Büchner, and C. G. Mitscherlich[1] showed that when the soln. is conc. by evaporation and cooled, it furnishes crystals of a basic salt. A similar product is obtained by crystallization from the filtrate from a mixture of soln. of mercuric chloride and silver nitrate. According to E. M. Walton, when a dry mixture of silver nitrate and mercuric chloride is triturated, the product appears moist owing to the formation of liquid mercuric nitrate.

N. A. E. Millon and R. Varet obtained large crystals of **hemihydrated mercuric nitrate,** $Hg(NO_3)_2.\frac{1}{2}H_2O$, by evaporating the soln. over sulphuric acid or quicklime; and the former also found that a mush of crystals is precipitated when fuming nitric acid is added to a soln. conc. as much as possible by evaporation. A. J. Cox prepared long transparent crystals of **monohydrated mercuric nitrate,** $Hg(NO_3)_2.H_2O$, by saturating 50 per cent. nitric acid with commercial mercuric nitrate, evaporating the soln. under diminished press., and drying the crystals by press. between filter paper. He found that if the conc. of free acid in the soln. is not less than 18·72*N*-HNO_3 at 25°, no basic salt crystallizes out. H. V. Regnault obtained clear colourless plates of what he regarded as **octohydrated mercuric nitrate,** $Hg(NO_3)_2.8H_2O$, by cooling to −15° a nearly neutral soln. conc. as much as possible by evaporation; but N. A. E. Millon showed that such a soln. has less water than is represented by the octohydrate. The great hygroscopicity of the crystals has possibly led to erroneous conclusions being drawn from the analytical work; and it has also prevented accurate measurements being made of the physical properties.

The **crystals** of the hemihydrate are simply described by R. Varet as being transparent; those of the monohydrate, by A. J. Cox, as being long and transparent; and those of the octohydrate, by H. S. Ditten, as clear, colourless rhombic plates. J. W. Retgers said that the **specific gravity** of mercuric nitrate (hemihydrated) is 4·3; and that the **melting point** is 79°. N. A. E. Millon said that the crystals of the hemihydrate are slowly decomposed giving off nitric acid when allowed to stand over conc. sulphuric acid. H. S. Ditten said that the octohydrate melts in a warm room; and A. Ditte added that after melting, it gives off water and nitric acid, and leaves behind a white powder which is decomposed by water into free acid and a yellow basic nitrate. P. W. Bridgman detected no signs of a transition into another form at 20° and increasing press. up to 12,000 kgrms. per sq. cm.; at 180° and 1000 kgrms. per sq. cm. press., the salt decomposed with explosive violence. J. Schröder and H. Steiner found **the raising of the boiling point** of soln. in methyl acetate corresponded with the **molecular weight,** $Hg(NO_3)_2$; F. M. Raoult also inferred the formula $Hg(NO_3)_2$ from **the freezing point of solutions** of mercuric oxide in nitric acid. R. Varet estimated the **heat of formation** to be $Hg_{liq.}+H_{2gas}+3O_{2gas}+\frac{1}{2}H_2O_{liq.}=Hg(NO_3)_2.\frac{1}{2}H_2O_{solid}+57·4$ to 58·36 Cals., and with the precipitated oxide and dil. nitric acid: $HgO+HNO_{3aq.}=Hg(NO_3)_2.\frac{1}{2}H_2O_{liq.}+7·3$ Cals. J. Thomsen gave $(Hg, O, 2HNO_{3aq.})=37·07$ Cals., and $(HgO, 2HNO_{3aq.})=6·4$ Cals. R. Varet gave for the **heat of solution** in dil. nitric acid, −0·7 Cal. The hydrolytic decomposition accounts for the low heat of soln. in spite of its being an endothermal reaction. S. M. Tanatar and L. Pissarjewsky found the heat of soln. in an aq. soln. of calcium chloride to be 11·545 Cals., and very small in alcohol; the heat of the reaction with an alcoholic soln. of sodium hydroxide is 19·864 Cals. R. Varet estimated that the reduction of mercuric to mercurous nitrate develops 9·9 Cals.

According to P. T. Muller and E. Carrière, the mean **specific refraction** of the soln. in 0·6*N*- to 1·05*N*-HNO_3 in yellow light is 0·0782, and the **specific dispersion** 0·0057. D. Gernez studied the **triboluminescence** of the crystals. F. Teltscher measured the eq. **electrical conductivity,** λ, of aq. soln. of mercuric nitrate, and found for n mols of the salt per litre:

n-$Hg(NO_3)_2$	0·0730	0·1460	0·1620	0·3420	0·1620
λ	114·0	124·5	110·0	133·5	144·5
n-HNO_3	0·029	0·059	0·011	0·0225	0·122
n-$Hg^{\cdot\cdot}$-ions	0·046	0·056	0·092	0·124	0·038

This scheme also shows the estimated hydrolysis and **degree of ionization** of soln. of mercuric nitrate. H. N. Morse also calculated the ionic conc. of soln. of mercuric nitrate. E. Abel agitated soln. of mercuric nitrate in 0·3N-HNO_3 until equilibrium was attained, and the conc. of the mercurous and mercuric salts in the soln. were determined on the assumption that these conc.. were nearly proportional to the conc. of the corresponding ions. The ratio $[HgNO_3]/[Hg(NO_3)_2]$ was found to be constant and nearly equal to 239·5 at 25°, showing that the two ions have the same valency, and that the reaction takes place in accord with the equation $Hg^{\cdot\cdot}+Hg=Hg{\cdot}Hg^{\cdot}$, where the mercurous ion consists of two atoms. R. Varet also assumed that soln. of mercuric nitrate in dil. nitric acid contained neither an acid nor a basic salt. H. N. Morse studied the **transport numbers.**

Some chemical properties of mercuric nitrate.—V. H. Veley [2] found that mercuric nitrate is reduced to mercurous nitrate by **hydrogen.** The hydrolytic action of **water** has been indicated above, and it is further discussed in connection with basic salts. W. Sievers found that with **chlorine,** hypochlorous and nitric acids, and mercuric chloride are formed; and that **bromine** acts similarly. According to J. Spiller, bromine has no action on mercurous salts. H. Saha and K. N. Choudhuri obtained a black substance by the action of aq. **ammonia**—*vide* the mercury ammonium nitrates. E. C. Franklin and C. A. Kraus found mercuric nitrate to be readily soluble in liquid ammonia; V. H. Veley found **nitric oxide** reduces a soln. of mercuric nitrate like hydrogen, and E. Divers and T. Haga, that nitric oxide, or an **alkali nitrite,** furnishes hydroxylamine. A. Ditte found that monohydrated **nitric acid** dissolves no octohydrated mercuric nitrate in the cold, and but traces when heated; H. Rose obtained a yellow precipitate by passing **phosphine** into a soln. of mercuric nitrate; the yellow precipitate then became white. When washed in water and dried over sulphuric acid, the yellow colour was restored. The composition is $P_2Hg_3.6HgO.3N_2O_5$. The compound explodes when heated or by percussion. B. E. Howard showed that **hypophosphorous acid** reduces the salt violently to the metal; and H. Erdmann and P. Köthner, that **acetylene** gives with aq. soln. of mercuric nitrate a white crystalline precipitate which again gives off acetylene when boiled with dil. acids, and when heated, or treated with conc. sulphuric acid, an explosion occurs; J. Schröder reported that mercuric nitrate is soluble in **pyridine;** W. Eidmann, in **methylal;** and A. Naumann, in **acetone.** G. C. Wittstein obtained a white precipitate with **potassium ferrocyanide,** and a yellow precipitate with **potassium ferricyanide.** R. Cowper found that a compound, $(C_2H_2Hg_3O_2)(NO_3)_2$, is formed when mercuric nitrate is treated with **alcohol.** When a soln. of mercuric nitrate is added to ordinary alcohol, **mercury fulminate,** with the empirical formula $HgC_2N_2O_2$, is obtained; silver nitrate furnishes a corresponding *silver fulminate*, AgCNO. The various modes of formation of these salts—principally its spontaneous formation from isonitromethane, $(CH_2)O.NO.Hg$, at 0°; and from formylchloride oxime, $H(Cl)C:NOH$, by the action of silver nitrate—and its reaction with dil. hydrochloric acid, whereby hydrogen cyanide is formed, have led to the view that the fulminates are salts of monobasic *fulminic acid*, HO—N=C, silver fulminate thus becomes AgO—N=C, and mercuric fulminate, $Hg(ONC)_2$. The decomposition of mercury fulminate has been studied by A. Langhans. Many complex compounds of mercuric nitrate with other organic compounds—dimethylethylene, trimethyl carbinol, salicylic acid, urea, thiourea, etc.—have been prepared by G. Denigès, H. Lajoux and A. Grandval, C. J. Lintner, H. Byasson, J. E. Reynolds, etc. According to W. Biltz and F. Zimmermann, a soln. of mercuric nitrate colours the freshly precipitated **hydrogels** of beryllium, magnesium, cadmium, lead, and erbium hydroxides, yellowish-red; those of zinc, aluminium, manganese, lanthanum, praseodymium, and neodymium, yellow;

while those of indium, zirconium, antimony, and bismuth gave no coloration. H. N. Morse has studied the solubility of the silver halides in aq. soln. of mercuric nitrate; H. Debray and H. W. F. Wackenroder found that **silver chloride, bromide, and iodide,** and **mercurous chloride** are readily dissolved; and J. Schlesinger, and H. W. F. Wackenroder found that **mercurous chloride, bromide, and iodide, mercuric iodide,** and **silver cyanide** and **thiocyanate** are readily dissolved. J. W. Retgers found molten **mercuric acetate** dissolves but little mercuric nitrate.

The basic compounds of mercuric nitrate.—G. F. Hildebrandt [3] reported that some of the products formerly described, though basic, appear to react acid to litmus. K. Thümmel observed that the hydrolysis of mercuric nitrate progresses further the greater the proportion of water employed. G. Watson represented them not as compounds of normal salt and base, but as derivatives of orthonitric acid. R. J. Kane, and P. Grouvelle reported several yellow basic salts which were probably mixtures. A. J. Cox investigated the various mercuric nitrates which can be formed in aq. soln. at 25°. The results are shown graphically in Fig. 40, when the ordinates represent the number of mols of $(H, Hg_{\frac{1}{2}})NO_3$ per litre of soln., and the abscissæ the increased basicity x of the solid phase $3Hg(NO_3)_2 - xN_2O_5$. A. J. Cox found only **mercuric dioxynitrate,** $2HgO.Hg(NO_3)_2$, to be formed in aq. soln. The limits of existence are with soln. between $18{\cdot}715N$-HNO_3 and $0{\cdot}159N$-HNO_3 at 25°; and $17{\cdot}930N$-HNO_3 and $0{\cdot}136N$-HNO_3 at 15°. It was washed with dil. nitric acid, pressed between filter paper, and dried in air at 95°. N. A. E. Millon obtained the same product by drying his monohydrate at 120°. The heavy white powder was found by N. A. E. Millon to begin to decompose at 260°, and the decomposition is vigorous at the b.p. of mercury. When continuously washed with cold water for some time, it appears pale pink, and the colour gradually deepens and approaches that of red mercuric oxide; boiling water acts more rapidly forming mercuric oxide, as was also noted by L. V. Brugnatelli and C. G. Mitscherlich. R. J. Kane, and J. Murray said that long boiling does not yield mercuric oxide alone; J. W. Döbereiner also obtained a very small yield of the oxide. N. A. E. Millon found an aq. soln. of alkali sulphate converts it into the basic sulphate; alkali chloride, forms a basic chloride; and alkali chromate, a basic chromate. N. A. E. Millon, and R. Varet claimed to have made the **monohydrated mercuric dioxynitrate,** $2HgO.Hg(NO_3)_2.H_2O$, by washing the basic nitrate, $HgO.Hg(NO_3)_2.H_2O$, or the normal nitrate with cold water. The former also obtained it by heating mercuric nitrate until it forms a pulverulent white mass, washing 7–8 times with cold water, and drying over sulphuric acid. It was claimed that 2·62 per cent. of water is lost at 120°. R. Varet gave for the heat of formation with precipitated mercuric oxide, $3HgO+2HNO_{3dil.}=3HgO.N_2O_5.H_2O_{solid}+15{\cdot}45$ Cals.; and $HgO.N_2O_5.\frac{1}{2}H_2O_{solid}+2HgO+\frac{1}{2}H_2O=3HgO.N_2O_5.H_2O_{solid}+8{\cdot}092$ Cals.

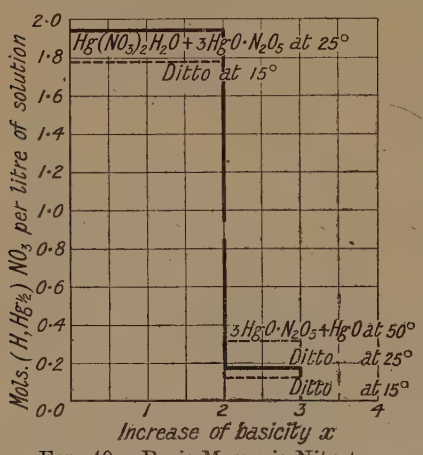

Fig. 40.—Basic Mercuric Nitrates.

N. A. E. Millon reported monohydrated **mercuric oxynitrate,** $HgO.Hg(NO_3)_2.H_2O$, to be formed by saturating nitric acid of sp. gr. 1·45 with mercuric oxide; and also by digesting yellow mercuric oxide for 50 days with an excess of an acidified soln. of mercuric nitrate. A. Mailhe also obtained it by the action of cupric hydroxide, $4CuO.H_2O$, or $CuO.H_2O$, or of nickel hydroxide, or carbonate on a cold soln. of mercuric nitrate; and also in clinorhombic prisms or plates by crystallization from cold sat. soln. of mercuric oxide in a soln. of uranyl nitrate, or in hot soln. of

aluminium nitrate, or ferric nitrate. It appears either as a yellow crystalline powder or in monoclinic prisms. It is possible that this salt is really the dihydrate, $HgO.Hg(NO_3)_2.2H_2O$, or $HO.Hg.NO_3.\frac{1}{2}H_2O$, obtained by C. G. Mitscherlich by evaporating and cooling an acidified soln. of mercuric nitrate. According to J. C. G. de Marignac, and C. F. Rammelsberg, the crystals are rhombic bipyramids with axial ratios $a : b : c = 0{\cdot}6976 : 1 : 0{\cdot}5186$. M. Donovan, and R. J. Kane found that this compound decomposes on exposure to moist air. The latter also obtained a yellow basic nitrate, $3HgO.N_2O_5.H_2O$, and mercuric oxide when treated with cold water, and finally, according to C. G. Mitscherlich, mercuric oxide alone. The aq. extract, said R. J. Kane, furnishes the original salt when evaporated and cooled. C. G. Mitscherlich found that the salt decomposes when heated into nitric acid and mercuric oxide, and, when triturated with sodium chloride and then with water, soluble mercuric chloride and an insoluble red oxychloride are formed. This basic nitrate dissolves in nitric acid. H. S. Ditten claimed to have obtained colourless needle-like crystals of a trihydrate, $HgO.Hg(NO_3)_2.3H_2O$, from the liquid obtained by melting octohydrated mercuric nitrate. K. Thümmel prepared a basic nitrate, $HgO.Hg(NO_3)_2$, with an undetermined amount of water, by adding sodium carbonate or hydrocarbonate to a soln. of mercuric nitrate.

B. Finzi found that freshly precipitated silver chloride is soluble in an aq. soln. of mercuric sulphate. The solubility increases (but not in proportion) with the amount of mercuric salt present, but it is increased more by dilution, so that the greatest amount of silver chloride is dissolved by a large excess of mercuric salt at considerable dilution. When to such a soln. hydrochloric acid is added in quantity eq. to the silver present, the metal is not all precipitated. The soln. probably contains **silver mercuric sulphatochloride.** Similar results are obtained when hydrochloric acid is added to a soln. of silver sulphate and mercuric sulphate. The soln. probably contains **silver mercuric sulphate.** The amount of silver chloride remaining dissolved increases with the amount of mercury present, but not proportionately. When the precipitated silver chloride has been filtered, the filtrate gives a further precipitate with hydrochloric acid or chlorides, and with silver nitrate, whilst sulphates, nitrates, and alkali acetates cause no precipitation. **Silver mercuric nitrate** and acetate have been similarly made. Similar phenomena have been observed with the mercuric nitrates and acetates. Yellow mercuric oxide dissolves in warm soln. of silver nitrate, sulphate, or acetate. A boiling soln. of silver sulphate, sat. in the cold, is treated with yellow mercuric oxide until no more dissolves. The filtered soln. deposits small rhombic tablets of pale yellow **silver mercuric oxysulphate,** $Ag_2SO_4.HgO$; a $2N$-soln. of silver nitrate, similarly treated, gives tufts of acicular crystals of reddish-yellow **silver mercuric oxynitrate,** $AgNO_3.2HgO$; and a hot almost sat. soln. of cupric nitrate, similarly treated, gives **cupric mercuric oxynitrate,** $Cu(NO_3)_2.HgO.3H_2O$, in pale blue acicular crystals.

Complex salts with mercuric nitrate.—There are some mixed basic nitrates which appear to contain both mercurous and mercuric oxides. F. Teltscher[4] measured the potential of mixed soln. of the two nitrates. P. C. Ray regards many of these mixed basic salts as containing the group $HO.Hg_2NO_3$ analogous with $Hg'_2(NO_3)_2$. He obtained a basic salt with the empirical composition, $2Hg_2O.HgO.N_2O_5.H_2O$, which can be regarded as an **oxymercurosic hydroxynitrate,** $HgO.2(HO.Hg_2NO_3)$. It was at first thought that this compound was a nitrite, but it was later shown to be a nitrate. This salt was prepared in orange-yellow crystalline masses by the evaporation of the mother liquor obtained in the preparation of mercurous nitrite: $4HgNO_2+Hg(NO_2)_2+H_2O=4NO+HgO.2Hg_2O.N_2O_5.H_2O$. P. C. Ray also prepared a second oxymercurosic hydroxynitrate, $HgO(HO.Hg'.NO_3)(HO.Hg'_2.NO_3)$—the former was designated the α-salt, and the latter the β-salt. The latter was obtained from the mother liquor remaining after the preparation of mercurous nitrite; by evaporating soln. of mercury in nitric acid, sp. gr. 1·11 to 1·2 at 35°; at 22°, the basic mercurous nitrate, $4Hg_2O.3N_2O_5.H_2O$, is formed.

H. Fürth reported a **mercurosic oxynitrate,** $HgO.Hg.NO_3$, to be formed when acetamide is treated with mercurous nitrate, or when a soln. of yellow mercuric oxide in an aq. soln. of mercurous nitrate is boiled until its colour becomes yellowish-green. C. F. Gerhardt, and T. Brooks prepared a substance with the same ultimate composition by dissolving 2 parts of mercury completely in 3 parts of boiling nitric acid of sp. gr. 1·2 ; and C. F. Gerhardt made it by melting mercurous nitrate whereby nitric oxide is given off. According to T. Brooks, the yellow powder decrepitates at 100°, and becomes dark yellow, but the colour becomes paler on cooling. Very little change occurs at 200°, red vapours are given off at 260°, and it becomes dark red, at a higher temp., when mercuric oxide is formed. It becomes brownish-red when triturated with sodium chloride, and water extracts some mercuric chloride from the mass. When boiled with water and exposed to air, the mercurous nitrate is oxidized to mercuric oxide and mercury, but if air be excluded, some mercuric nitrate and a trace of mercurous nitrate dissolve, and the insoluble residue contains both oxides ; and when digested with barium carbonate and water, all the nitric acid appears in the aq. soln. H. Fürth found that his product is blackened with ammonia ; and it gives off no ammonia when digested with a soln. of sodium sulphide and hydroxide.

H. Rose [5] and D. Vitali made **mercuric nitratodisulphide,** $Hg(NO_3)_2.2HgS$, by passing insufficient hydrogen sulphide into a soln. of mercuric nitrate, to precipitate all the mercury as sulphide. The precipitate was quickly washed with cold water. N. Tarugi added thioacetic acid to a cold soln. of mercuric nitrate ; extracted the washed and dried precipitate with carbon disulphide ; and dried the product in vacuo. C. Barfoed made it by treating the precipitate obtained by the action of hydrogen sulphide on a mercurous salt, with a soln. of mercuric nitrate, or with cold fuming nitric acid, or hot dil. nitric acid ; or, according to J. L. Howe, with boiling acid of sp. gr. 1·42 and a drop of dil. hydrochloric acid (1 : 3). If 10 drops of hydrochloric acid is added, the whole is dissolved. Only a trace of sulphuric acid, but much mercuric nitrate, is produced. The product is washed until free from acid, and dried first at 40°–50°, and then at 100°. K. Heumann treated cinnabar containing free mercury with dil. nitric acid ; R. Palm digested black mercuric sulphide with a soln. of mercuric nitrate ; R. Palm also treated a soln. of black mercuric sulphide in one of mercuric acetate with nitric acid or an alkali nitrate ; and N. Tarugi treated mercuric thioacetate with warm conc. nitric acid. The nitratodisulphide is a white powder which when heated in a tube was found by H. Rose to decompose into nitrous fumes, sulphur trioxide, mercury, and mercuric sulphide. When boiled with water, C. Barfoed found it to acquire a grey colour, but very little dissolves ; he also stated that it dissolves in hydrochloric acid, with the evolution of nitric oxide, the separation of sulphur, and the formation of sulphuric acid. H. Rose found that it is decomposed by hot aqua regia, forming sulphuric acid, and he stated that when suspended in water, and treated with hydrogen sulphide, it is converted into mercuric sulphide and nitric acid. According to C. Barfoed, when heated with sulphuric acid, of sp. gr. 1·84, it gives off sulphur dioxide, and is transformed into mercuric sulphate ; if the sulphuric acid contains a little water, nitric acid and no sulphur dioxide are formed—mercuric sulphate and sulphide are produced. N. Tarugi found that the nitratodisulphide is blackened by ammonia. H. Rose said that it is not decomposed by nitric acid ; N. Tarugi, that it is slightly decomposed ; and J. L. Howe, that it dissolves if the nitric acid contains a small proportion of hydrochloric acid. According to K. Haack, cold soln. of sodium hydrophosphate or hydroarsenate act slowly on mercuric sulphatodisulphide, and hot soln. form black mercuric sulphide ; it is also decomposed by phosphoric and arsenic acids, and by sodium dihydrophosphate and dihydroarsenate. H. Rose said that cold aq. soln. of the alkali carbonates gradually change the colour yellow and finally black ; with boiling soln., the compound is blackened at once.

F. Gramp prepared a complex product $HgO.6HgS.2Hg(NO_3)_2.12H_2O$, by heating to

120° in a sealed tube a mixture of cinnabar, or, better, the black sulphide with nitric acid of sp. gr. 1·2. The white crystalline product loses seven mols of water at 150°. It is insoluble in water, and in cold nitric acid of sp. gr. 1·2, the hot acid attacks the product and leaves a residue of mercuric sulphide. It is decomposed by a soln. of sodium chloride, forming mercuric sulphide and chloride, and sodium nitrate and hydroxide. It is gradually blackened by potassium hydroxide.

C. Kosmann[6] prepared **ammonium mercuric nitratotetrachloride,** $NH_4NO_3.2HgCl_2$, by the action of cold. conc. nitric acid on mercuric amidochloride, and warming the soln. On evaporation silvery-white plates are formed. Water does not dissolve the crystals, but the liquid gradually becomes turbid; a boiling soln. of potassium hydroxide gives only a little ammonia; ether extracts much mercuric chloride. K. A. Hofmann and E. C. Marburg passed nitric oxide into a cold soln. of mercuric diammino-chloride in absolute alcohol. The soln. is conc. by evaporation, and colourless needles of **diammonium mercuric dinitratodichloride,** $2NH_4NO_3.HgCl_2$, are obtained by adding methyl alcohol. The aq. soln. is strongly acid; it gives ammonia when heated with potassium hydroxide; and chlorine with hot sulphuric acid. V. Borelli did not isolate **mercuric nitratochloride,** $NO_3.Hg.Cl$, but he deduced its existence from the conductivity of a soln. of mercuric nitrate containing mercuric chloride. H. N. Morse obtained **mercuric nitratobromide,** $NO_3.Hg.Br$, from a soln. of the component salts. V. Borelli obtained what he regarded as crystals of **mercuric nitratoiodide** by cooling a conc. soln. of mercuric chloratoiodide in conc. nitric acid. The 1 : 1 iodide, $Hg(NO_3)_2.HgI_2$, or $NO_3.Hg.I$, was prepared by J. Preuss by mixing a boiling soln. of mercuric nitrate of sp. gr. 1·35 with enough nitric acid to prevent it becoming turbid in water, and an excess of iodine, when white tabular crystals separate on cooling; W. Sievers used mercuric iodide in place of iodine. A. Souville, C. H. Hirzel, K. Kraut, treated a soln. of mercurous or mercuric iodide with hot nitric acid; half the iodine volatilizes, some nitrous fumes are evolved, and the crystals were pressed between paper since they are decomposed by washing with water or alcohol—E. Riegel said that the decomposition is less with ether. P. Lemoult obtained crystals of the same salt by the action of nitric acid on mercuric iodophosphide, Hg_3I_3P. The crystals melt when heated, and give off nitrous fumes, mercuric iodide volatilizes, and mercuric oxide remains. The crystals are rapidly decomposed by water, forming mercuric iodide, and soluble mercuric nitrate; A. Souville found that alcohol of sp. gr. 0·814 decomposes the salt; and E. Riegel stated that the decomposition is less with ether. According to J. Preuss, an aq. soln. of ammonia or potassium hydroxide separates mercuric oxide, and ammonium or potassium mercuric iodide is formed. J. von Liebig reported the formation of small red crystals of $Hg(NO_3)_2.2HgI_2$ during the cooling of a boiling and filtered soln. of mercuric iodide with potassium nitrate. It is stated by E. Riegel that the salt is decomposed into its components by water. By dissolving some mercuric iodide in the hot filtrate from the preceding salt, E. Riegel claimed to have made acicular crystals of $2Hg(NO_3)_2.3HgI_2$, but K. Kraut failed to obtain any such salt.

Double salts.—H. L. Wells and H. P. Beardsley[7] believed that **cæsium mercuric nitrate,** possibly $CsNO_3.Hg(NO_3)_2$, existed in a soln. of the component salts; but they did not succeed in its isolation. K. Klinger reported the formation of a basic salt, **calcium mercuric oxynitrate,** by allowing a hot sat. soln. of calcium nitrate to stand a long time in contact with red mercuric oxide. G. Städeler obtained white octahedral (cubic) crystals of **barium mercurous oxynitrate,** $2BaO.2Hg_2O.3N_2O_5$, by mixing soln. of the component salts. The crystals are colourless if produced in soln. free from acid and in darkness; in light or in acidic soln. the crystals have a yellow colour, and they become greenish-brown. They can be recrystallized colourless from nitric acid soln. The crystals are decomposed by water which abstracts barium nitrate, and leaves a yellowish-green residue. The salt is very soluble in hot dil. nitric acid. The corresponding **strontium mercurous oxynitrate,** $2SrO.2Hg_2O.3N_2O_5$, was prepared in an analogous manner, and it is much more soluble than the corresponding barium salt.

A. Mailhe obtained blue plates or prisms of dihydrated **cupric mercuric oxynitrate,** $CuO.Hg(NO_3)_2.2H_2O$, from a soln. of mercuric oxide in a warm soln. of cupric nitrate; by working with cold. soln. he obtained blue plates of the tetrahydrate, $CuO.Hg(NO_3)_2.4H_2O$; and by adding yellow mercuric oxide to a conc. soln. of cupric nitrate, or by cooling a boiling soln. of mercuric oxide in a 4*N*-soln. of cupric nitrate, he obtained a blue powder consisting of quadratic prisms or plates of the pentahydrate, $CuO.Hg(NO_3)_2.5H_2O$. All the salts are readily decomposed by water with the separation of mercuric oxide. B. Finzi prepared pale blue acicular crystals of **cupric mercuric oxynitrate,** which he regarded as $Cu(NO_3)_2.HgO.3H_2O$, by cooling a filtered soln. obtained by boiling mercuric oxide in an almost sat. soln. of cupric nitrate. The crystals can be preserved unchanged in a desiccator; they lose water at 100°; they are decomposed by water with the separation of mercuric oxide; they are soluble in nitric, sulphuric, and hydrochloric acids. The aq. soln. gives the characteristic reactions of mercuric and cupric salts, and when treated with potassium hydroxide, it becomes green without the separation of mercuric or cupric oxide. The addition of aq. ammonia forms an intense blue soln., and a white powder of ammonium mercuric nitrate. B. Finzi also prepared needle-like crystals of **silver mercuric oxynitrate,** $AgNO_3.2HgO$, in a similar way. The crystals turn black on exposure to light; they are decomposed by water; they are soluble in nitric or sulphuric acid; with sodium thiosulphate, silver and mercuric thiosulphates, sodium nitrate, and sodium hydroxide are formed; mercuric iodide produces silver and mercuric iodides, and potassium nitrate and hydroxide. J. J. Berzelius reported columnar crystals of $2AgNO_3.Hg(NO_3)_2$, soluble in water without decomposition; and P. C. Ray obtained a series of silver mercuric oxynitrates with $(Hg^{\cdot}, Ag^{\cdot}) : Hg^{\cdot\cdot} : NO_3$ in the ratios 4 : 1 : 2; 4 : 1 : —; 7 : 1 : 8; 2 : 1 : 2; and 1·8 : 1 : 1·7, by rubbing mercurous nitrite with silver nitrate and the least possible quantity of water to form a mush, treating the mass with water, and evaporating the filtered soln. under reduced press. Lemon-yellow microscopic crystals are formed.

A. Mailhe prepared white quadratic crystals of **monohydrated zinc mercuric oxynitrate,** $ZnO.Hg(NO_3)_2.H_2O$, by cooling a hot soln. of mercuric oxide in a conc. soln. of zinc nitrate; and acicular or monoclinic prisms of the dihydrate, $ZnO.Hg(NO_3)_2.2H_2O$, by adding zinc oxide to a conc. soln. of zinc nitrate. Water decomposes both salts with the separation of mercuric oxide. He also obtained white hexagonal prisms of **dihydrated cadmium mercuric oxynitrate,** $CdO.Hg(NO_3)_2.2H_2O$, by cooling a hot soln. of mercuric oxide in a conc. soln. of cadmium nitrate; and white monoclinic prisms or plates of the trihydrate, $CdO.Hg(NO_3)_2.3H_2O$, from a soln. of mercuric oxide in a soln. of cadmium nitrate. Both salts are decomposed by water.

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§ 36. Ammonium Mercuric Compounds

According to A. F. de Fourcroy [1] (1792), a soln. of mercuric nitrate gives a white precipitate with ammonium nitrate, and on evaporating the filtered soln., six-sided crystals appear. L. Pesci prepared colourless crystals of **mercuric diamminonitrate,** $Hg(NH_3)_2(NO_3)_2$, by the action of a 50 per cent. soln. of ammonium nitrate upon the so-called Mitscherlich's salt—*vide infra*—or on a mercuric monoxynitrate, $HgO.Hg(NO_3)_2$. D. Strömholm also made plate-like crystals by mixing 6 grms. of mercuric nitrate dissolved in 2 c.c. of $4N$-HNO_3 with enough water to make 10 c.c. ; and then added 11 c.c. of 8 per cent. aq. ammonia, and 50 c.c. of 50 per cent. ammonium nitrate. L. Pesci formulated the salt $3NH_4NO_3.NHg_2NO_3$, *ammonium dimercuriammonium nitrate ;* E. C. Franklin regarded it as the diammino-salt. The

crystals are not changed by exposure to light, with cold water the salt forms $NH_4NO_3.3NHg_2NO_3.2H_2O$, and with boiling water ammonium mercuric nitrate; it is soluble in aq. ammonia, and the soln. on evaporation furnishes $NH_4NO_3.NHg_2NO_3.H_2O$.

D. Strömholm mixed 6 grms. of mercuric nitrate dissolved in 2 c.c. of $4N$-HNO_3, and diluted with water to 10 c.c., with 11 c.c. of 8 per cent. aq. ammonia and 50 c.c. of 10–20 per cent. soln. of ammonium nitrate. The small octahedral crystals have the composition of **monomercuriammonium nitrate,** $NH_2.Hg.NO_3$—the nitrate corresponding with infusible white precipitate, $NH_2.Hg.Cl$. When treated with warm water they form the nitrate of Millon's base.

The ammonio-base, **dimercuriammonium nitrate**, $Hg_2N.NO_3$, was prepared by L. Pesci and C. F. Rammelsberg by the action of dil. nitric acid on Millon's base, while L. Pesci, and K. A. Hofmann and E. C. Marburg prepared it by the action of a slight excess of aq. ammonia on an aq. soln. of mercuric nitrate. L. Pesci also obtained it by washing mercuric diamminonitrate with hot water. C. F. Rammelsberg made it by heating mercuric oxide with a soln. of ammonium nitrate; and D. Strömholm by shaking monomercuriammonium nitrate with warm water. The salt is a pale yellow powder, insoluble in water, and yields no ammonia when boiled with potassium hydroxide. P. C. Ray could not obtain the anhydrous compound; but what was regarded as a hemihydrate, $NHg_2NO_3.\frac{1}{2}H_2O$, was shown by E. C. Franklin to be more probably the monohydrate, *i.e.* the nitrate of Millon's base; it is also called Soubeiran's salt, is **mercuric hydroxyamidonitrate,** $HO.Hg.NH.HgNO_3$, or, according to K. A. Hofmann and E. C. Marburg, *oxydimercuriammonium amidonitrate*; $OHg_2 : NH_2NO_3$. P. C. Ray prepared his hemihydrate as a white amorphous powder by the action of conc. nitric acid on dimercuriammonium nitrite, NHg_2NO_2; and, according to E. Soubeiran and R. J. Kane, by adding a slight excess of dil. aq. ammonia to a soln. of mercuric nitrate containing the least possible quantity of acid. K. A. Hofmann and E. C. Marburg made the monohydrate by digesting Millon's base with 10 per cent. nitric acid; washing with water acidified with less and less nitric acid, then with alcohol, and ether; and finally drying in vacuo. H. Fürth made it by the action of ammonium nitrate on mercuric acetamide; or by the action of dil. nitric acid on the precipitate obtained by adding aq. ammonia to mercuric acetamide. R. J. Kane obtained it by boiling mercuric monomercuriammonium hydroxyamidonitrate with water. The white powder was found by E. Soubeiran, and R. J. Kane to become yellow when heated; it then gives off ammonia, nitrogen, and nitrous fumes; and finally oxygen and mercury; it is not decomposed, nor is ammonia evolved when it is boiled with potassium hydroxide; with hydrogen sulphide it forms mercuric sulphide and a neutral soln. of ammonium nitrate; nitrous fumes are given off when it is boiled with hydrochloric acid, but it is soluble in the cold acid, and reprecipitated by water; and it is sparingly soluble without decomposition in nitric and sulphuric acids. It is soluble in aq. ammonia and partially precipitated when water is added. P. C. Ray found his product to be sparingly soluble in nitric acid, and to detonate suddenly when heated in a tube, forming nitrous fumes, mercury, steam, and a reddish-yellow residue principally mercuric oxide. According to L. Pesci, E. Soubeiran's *protonitrate ammoniaco-mercuriel* is probably a mixture of Soubeiran's salt and mercury.

The so-called *Mitscherlich's salt* was obtained by C. G. Mitscherlich by treating a soln. of mercuric nitrate, acidified with as little nitric acid as possible, with dil. ammonia, not in excess, and drying at 100°; he also obtained it by boiling the basic nitrate $2HgO.Hg(NO_3)_2$ with a soln. of ammonium nitrate. L. Pesci also obtained it by the action of water on mercuric diamminonitrate. L. Pesci represents the formula as $NH_4NO_3.3NHg_2NO_3.2H_2O$, *dihydrated ammonium-dimercuriammonium nitrate;* it has also been represented as *mercuriammonium oxydimercuriammonium nitrate,* $NH_2HgNO_3.NH_2(HgOHg)NO_3$; while E. C. Franklin regards it as **mercuric monomercuriammonium hydroxyamidonitrate,** $NH_2HgNO_3.HOHg.NH.HgNO_3$. The white powder behaves like Soubeiran's salt when heated, and when treated with

potassium hydroxide ; according to R. J. Kane, when heated with water, it forms Soubeiran's salt ; and, according to L. Pesci, when boiled with water, it forms dimercuriammonium nitrate. It is decomposed when heated to 100°, and is readily soluble in a soln. of ammonium nitrate. The salt was analyzed by M. C. Lea, L. Pesci, C. G. Mitscherlich, R. J. Kane, and J. S. F. Pagenstecher.

A compound with the empirical composition $Hg_2N_2H_6O.2NO_3$, was prepared by C. G. Mitscherlich by evaporating a soln. of Mitscherlich's salt or Soubeiran's salt in one of ammonium nitrate until crystallization occurs ; J. C. F. Meyer made it by evaporating the soln. formed by adding a soln. of ammonia or ammonium carbonate to one of mercuric nitrate until the precipitate first formed is redissolved ; L. Pesci also obtained it by super-saturating a dil. soln. of mercuric nitrate with ammonia—a similar process gave J. S. F. Pagenstecher a more basic product, *vide infra*. L. Pesci represented the composition by the formula $NHg_2NO_3.NH_4NO_3.H_2O$; *hydrated ammonium dimercuriammonium nitrate ;* it can also be regarded as *oxymercuriammonium diamminonitrate*, $(NH_3)_2(HgOHg)(NO_3)_2$; and E. C. Franklin represents it as *hemihydrated mercuric amidonitrate*, $NH_2.Hg.NO_3.\frac{1}{2}H_2O$, or as **mercuric diamminoxynitrate,** $Hg(NO_3)_22NH_3.HgO$. L. Pesci found that the yellowish octahedral crystals lose very little water at 115°–120°, but are decomposed at a higher temp. C. G. Mitscherlich said that the compound is easily decomposed by alkali hydrosulphides, and by hydrochloric acid, but not by other acids—sulphuric acid has no action, and the salt is very slightly soluble in nitric acid ; soln. of ammonia and potassium hydroxide are without action, and it is decomposed with difficulty by baryta water.

G. C. Wittstein found that mercuric oxide dissolves in a large excess of a soln. of ammonium nitrate, forming a compound which is not precipitated by ammonia ; mercurous oxide behaves in a similar way, but with the separation of mercury. R. J. Kane prepared what is known as *Kane's salt* by dissolving Soubeiran's salt, or mercuric oxide in a boiling soln. of ammonium nitrate, and on allowing the soln. to cool, small shining needles are obtained ; he made the same salt by boiling mercuric nitrate with a soln. of ammonium nitrate. L. Pesci prepared the same salt, and represented its composition by $2NH_4NO_3.NHg_2NO_3.2H_2O$, or *dihydrated diammonium dimercuriammonium nitrate ;* or as *hydrated diammonium oxymercuriammonium nitrate*, $2NH_4NO_3.NH_2(HgOHg)NO_3.H_2O$; or by E. C. Franklin, as **dihydrated mercuric monomercuriammonium diamminonitrate,** $Hg(NO_3)_2.2NH_3.2H_2O.NH_2HgNO_3$. R. J. Kane stated that water extracts ammonium nitrate from the crystals and leaves the salt $NH_2(HgOHg)NO_3$; and L. Pesci, that when heated to 110°–115°, it loses a mol of water, forming *monohydrated diammonium dimercuriammonium nitrate*, $2NH_4NO_3.NHg_2NO_3.H_2O$; which E. C. Franklin represents as **monohydrated mercuric monomercuriammonium diamminonitrate,** $Hg(NO_3)_2.2NH_3.H_2O.NH_2HgNO_3$.

J. S. F. Pagenstecher and R. J. Kane obtained a pale yellow precipitate of *oxytrimercuriammonium nitrate*, $NH_2(HgO.HgO.Hg)NO_3$, by adding a very large excess of ammonia to a soln. of mercuric nitrate. E. C. Franklin represented the product by the formula $HgO.HOHg.NH.HgNO_3$, **mercuric oxyhydroxyamidonitrate**—but he believed that *Pagenstecher's salt* is really a mixture of two salts.

C. H. Hirzel prepared a white earthy powder with a composition corresponding with $NHg(HgO.HgO.Hg)HgNO_3$, *mercuric oxytrimercuriammonium nitrate ;* which E. C. Franklin symbolized $4HgO.Hg(NO_3)_2.2NHg_2NO_3$, **mercuric dimercuriammonium tetroxynitrate.** He rubbed 9 mols of freshly precipitated mercuric oxide with a conc. soln. of 4 mols of ammonium nitrate ; then heated the mixture to the b.p., filtered rapidly, washed with boiling water, and dried the product. L. Pesci used a 40 per cent. soln. of ammonium nitrate and obtained dimercuriammonium nitrate. He was unable to make C. H. Hirzel's product. According to C. H. Hirzel, the product becomes yellow when heated, then decomposes suddenly with a hissing noise ; there is an evolution of red nitrous fumes, and the sublimation of a reddish-brown substance—very little water is produced. A boiling soln. of potassium hydroxide colours it yellow, and ammonia is evolved ; baryta water acts slowly, and all the nitrogen is gradually evolved as ammonia ; it is insoluble in nitric acid ; it gradually dissolves in a hot conc. soln. of ammonium nitrate, and with hydrochloric acid, a voluminous white precipitate is formed which dissolves when the mixture is warmed.

P. C. Ray reported a salt with the empirical formula $Hg_4N_2H_2O.2NO_3$, to be produced by the action of nitric acid on dimercuriammonium nitrite, $Hg_2N.NO_2$. E. C. Franklin regarded it as **mercuric dimercuriammonium hydroxyamidonitrate,** $Hg_2NO_3.HOHg.NH.HgNO_3$.

H. Saha and K. N. Choudhuri obtained a white amorphous powder with the empirical formula $N_2Hg_2H_4O_5$, which can be rearranged $NH_4NO_3.2HgO$, **mercuric ammonium oxynitrate,** by adding an excess of aq. ammonia to mercurous nitrate, evaporating the filtered soln. in vacuo over conc. sulphuric acid, washing with distilled water, and drying over calcium chloride. The product does not lose weight on the water-bath ; but when heated in a tube it decomposes explosively giving off nitrous fumes and ammonia. It is very stable, and is but slightly affected when boiled many days with a soln. of potassium hydroxide.

C. Barfoed obtained a product with the empirical formula $HgO.2NH_2HgNO_3$, **monomercuriammonium oxynitrate,** by adding a very slight excess of dil. aq. ammonia to a dil. feebly acid soln. of mercurous nitrate, and drying the washed product at 100°. It is soluble in acetic acid, and gives off ammonia when heated with a conc. soln. of potassium hydroxide. H. Saha and K. N. Choudhuri obtained the preceding compound by following C. Barfoed's instructions.

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§ 37. Mercury Phosphates

C. F. Gerhardt [1] and P. L. Dulong found that when sodium hydrophosphate, Na_2HPO_4, is added to a soln. of mercurous nitrate, a white crystalline precipitate of **mercurous phosphate,** Hg_3PO_4, is produced. K. Haack dropped a cold soln. of one mol of mercurous nitrate into a cold soln. of a mol of sodium hydrophosphate, washed the precipitate with cold water, and dried it in air. If the mercurous nitrate be in excess, C. F. Gerhardt reported that mercurous nitratophosphate is produced, and K. Haack, a basic *mercurous nitratophosphate.* The following remarks by old observers may refer to mercurous phosphate or to the nitrato-phosphate. When the phosphate is heated in a tube, C. F. Gerhardt and P. L. Dulong found that it fuses and gives off mercury leaving a yellow glass of mercuric phosphate. The salt is said to be insoluble in water ; R. Behrend measured the electromotive force of mercurous phosphate. H. Rose stated that when the salt is boiled with water, soluble mercuric phosphate and a grey mixture of mercury and the undecomposed salt are formed. According to J. B. Trommsdorff, hydrochloric acid colours the undecomposed salt grey, and black with a boiling soln. Aq. sulphurous acid or phosphorous acid slowly reduces the salt to mercury. The salt is said to be insoluble in an aq. soln. of phosphoric or tartaric acid and a cold soln. of potassium hydroxide decomposes the salt but no mercury passes into soln. ; but a little mercury is taken up when the salt is decomposed by a hot soln. of potassium carbonate. R. H. Brett found the salt dissolves imperfectly in a soln. of ammonium chloride ; G. C. Wittstein found that with an aq. soln. of ammonia or ammonium carbonate, the filtrate contains phosphoric acid and mercuric oxide, and a residue with mercury, mercurous and mercuric oxides, and ammonia.

J. Jacobsen prepared the double salt **silver mercurous phosphate,** $AgHg_2PO_4$, by adding a soln. containing a mol of sodium hydrophosphate to a mixed soln. with one mol of silver nitrate, and two mols of mercurous nitrate acidified with 2 per cent.

of nitric acid. The yellowish-white rhombic prisms or plates are blackened by ammonia with the liberation of some mercury.

C. F. Gerhardt reported monohydrated **mercurous nitratophosphate,** $HgNO_3.Hg_3PO_4.H_2O$, to be formed when an excess of sodium hydrophosphate is poured into an acid soln. of mercurous nitrate; the precipitate at first disappears as soon as formed, but is afterwards permanent; it is then washed with cold water. The white or yellowish-white powder consists of minute plates. When heated in a tube it gives mercuric oxide and red fumes. According to C. F. Gerhardt, if the mercurous nitrate soln. be poured into an excess of one of sodium hydrophosphate, the amorphous precipitate is normal mercurous phosphate. K. Haack reported a pale yellow basic salt—**mercurous oxynitratophosphate,** $Hg_2O.2HgNO_3.5Hg_3PO_4.H_2O$—to be formed when a cold soln. with one mol of sodium hydrophosphate is dropped into one with 9 mols of mercurous nitrate, and the product washed with cold water, and dried in air—*vide supra*.

A white precipitate of **mercurous pyrophosphate** is obtained when sodium or ammonium pyrophosphate is added to a soln. of a mercurous salt. According to H. Rose, however, when the two salts are triturated with cold water, a blackish precipitate is obtained, and a mercurous salt free from mercuric compounds passes into soln., but with boiling water, the precipitate is blacker still, and the soln. contains both mercurous and mercuric phosphates. According to A. Schwarzenberg, the white precipitate indicated above is a crystalline powder which leaves a residue of mercuric metaphosphate when ignited. F. Stromeyer said that mercurous pyrophosphate is soluble in an excess of the sodium pyrophosphate, but L. Gmelin said that it is neither blackened nor dissolved by an excess of the sodium salt. A. Schwarzenberg found that when freshly precipitated the salt is soluble in the soln. of sodium pyrophosphate, but when dried at 100°, mercurous pyrophosphate is insoluble in that menstruum; and when the mixture is boiled, the mercurous pyrophosphate blackens. He also found that the salt is decomposed by hydrochloric acid, is dissolved by nitric acid. T. Brooks stated that mercurosic oxide is decomposed in the dark by a cold soln. of sodium pyrophosphate, and the resulting salt—possible **mercurosic pyrophosphate**—is very unstable and blackens with hot water.

According to C. G. Lindbom, a pale yellow amorphous precipitate of **mercurous oxytrimetaphosphate,** $Hg_3P_3O_9.Hg_2O$, is obtained by mixing soln. of mercurous nitrate and of sodium trimetaphosphate. H. Lüdert added sodium hexametaphosphate to one of mercurous nitrate and obtained a white precipitate which, when washed with water and dried at 100°, corresponded with **mercurous hexametaphosphate,** $Hg_6P_6O_{18}$. The precipitate is soluble in an excess of the precipitant, and it is insoluble in water but soluble in acids.

According to H. Rose, and K. Haack, sodium hydrophosphate precipitates white **mercuric phosphate,** $Hg_3(PO_4)_2$, from a strongly acidified soln. of mercuric nitrate; with mercuric sulphate, no precipitation occurs, and with mercuric chloride a precipitate is very slowly formed in the cold, and a compact red precipitate is rapidly formed in hot soln. If an excess of sodium hypophosphate is used the precipitate is yellow and the colour gradually turns brown. Mercuric cyanide soln. are not precipitated by sodium hypophosphate. K. Haack also obtained the salt by dropping phosphoric acid into an excess of a soln. of mercuric nitrate, and also by boiling basic mercuric sulphate with a soln. of sodium pyrophosphate, and extracting the mercuric oxide with acetic acid. C. F. Gerhardt obtained normal mercuric phosphate by feebly calcining the mercurous salt.

The white precipitate, said J. B. Trommsdorff, and C. F. Gerhardt, is crystalline; and K. Haack obtained it in small lustrous needles by cooling hot soln. The salt assumes a transient yellow colour when heated, and the air-dried salt loses no water at 100°. J. B. Trommsdorff added that the salt sinters together when heated, and fuses into a yellow glass; if heated more strongly, it gives off mercury, oxygen, and phosphorous oxide. G. C. Wittstein found the salt to be insoluble in water

and in alcohol, but K. Haack said that the salt is soluble in hot water. A. Barillé found the salt to be soluble in an aq. soln. of carbon dioxide. K. Haack could not prepare a *basic salt* by boiling the basic sulphate with an excess of sodium hydrophosphate soln., for the sulphuric acid was completely removed and a mixture of normal mercuric phosphate and mercury was produced. L. Gmelin said that mercuric phosphate dissolves in phosphoric acid; but K. Haack contradicted this statement. J. von Liebig found that phosphorous or sulphurous acid reduces the salt to mercury—the reaction is slow and incomplete. According to J. B. Trommsdorff, cold dil. hydrochloric acid dissolves the salt slowly, while the hot dil. acid dissolves it rapidly; the cold conc. acid also dissolves the salt rapidly and copiously with the evolution of heat. When the hydrochloric acid soln. is treated with stannous chloride, mercury and stannic phosphate are formed; and on evaporating the hydrochloric acid soln. to dryness, hot alcohol extracts mercuric chloride from the product—hence, hydrochloric acid abstracts mercuric oxide from phosphoric acid. A soln. of hydrochloric acid abstracts the phosphoric acid, and a soln. of potassium hydroxide also extracts all this acid from mercuric phosphate without dissolving mercuric oxide; while a soln. of potassium carbonate takes up part of the acid, and at the same time dissolves some mercury oxide which is not precipitated when the soln. is boiled. According to J. von Liebig, mercuric phosphate redissolves when sodium chloride is added to the mother liquid in which it has been formed, but the crystalline salt dissolves with difficulty. K. Haack found that the solubility in a soln. of sodium or potassium chloride is limited by the conc. of the nitric acid liberated during the reaction, and if the acid is removed, the precipitate is converted into a basic chloride. G. C. Wittstein found that aq. ammonia extracts from the salt a little mercuric oxide and phosphoric acid, the salt is also soluble in soln. of ammonium carbonate, sulphate, or nitrate; and J. B. Trommsdorff found one part of the salt dissolves completely in a hot soln. of six parts of ammonia, and the soln. reddens litmus. T. Brooks obtained **mercurosic oxyphosphate,** $7Hg_2O.14HgO.2P_2O_5.2OH_2O$, by the action of a conc. warm, but not boiling, soln. of sodium hydrophosphate on powdered mercurosic nitrate, and washing the product with cold water. The salt blackens superficially when exposed to the air; it does not lose water at 100°, but is completely decomposed at a higher temp.

According to A. Schwarzenberg, a soln. of mercuric nitrate gives a white or yellowish-red precipitate with sodium pyrophosphate. When dried at 100°, the composition is that of **mercuric pyrophosphate,** $Hg_2P_2O_7$. A. Reynoso obtained a basic chloride by boiling a soln. of mercuric chloride with sodium pyrophosphate. Mercuric pyrophosphate is insoluble in an excess of the sodium salt; it is soluble in acids; decomposed by potassium hydroxide; and dissolves in an aq. soln. of sodium chloride like mercuric phosphate. T. Fleitmann and W. Henneberg found sodium trimetaphosphate gave a slowly forming precipitate with mercuric nitrate—presumably **mercuric trimetaphosphate.** F. Warschauer heated mercuric oxide or mercuric nitrate with an excess of phosphoric acid to 400°, and obtained what was thought to be **mercuric tetrametaphosphate.** According to H. Rose, sodium hexametaphosphate gave a white precipitate or oily mass with mercuric nitrate, but not with mercuric chloride. P. Glühmann said that a conc. soln. of mercuric chloride gives a turbidity with soln. of sodium triphosphate, and when shaken with an excess of the latter, an amorphous powder is obtained which in a few days appears to be strewn with black crystals—possibly **sodium mercuric triphosphate.** According to H. Lüdert, the product is **mercuric hexametaphosphate,** $Hg_3P_6O_{18}$. The oily mass when dried in air forms a colourless translucent glass which after trituration and drying at 100°, appears like glue. The undried fresh precipitate is soluble in water, but the dried precipitate is but sparingly soluble. It is readily soluble in acids.

P. C. Ray [2] prepared a white crystalline powder of what he regarded as *dimercuriammonium hydrophosphate,* $NHg_2.H_2PO_4$, and E. C. Franklin as **mercuric**

monomercuriammonium phosphate, $NH_2.Hg.HgPO_4$, by heating dimercuriammonium nitrite with phosphoric acid for 2–3 days at 50°–60°, washing, and drying in the steam-bath. C. H. Hirzel digested freshly precipitated mercuric oxide with a soln. of ammonium hydrophosphate for some days in the cold, or for a less time when warmed, and obtained a white powder of what he regarded as *mercuric oxymercuriammonium phosphate*, $Hg\{NH_2(HgOHg)\}PO_4$; C. F. Rammelsberg, as *mercuric oxyamidophosphate*, $NH_2.Hg.PO_4 : Hg.HgO$; and E. C. Franklin, as **mercuric hydroxyamidophosphate,** $Hg : PO_4Hg.NH.HgOH$. It is stable in air; it becomes yellow when heated and the white colour is restored on cooling; it melts at a higher temp. and decomposes with the evolution of water, ammonia, and mercury vapour, and if the decomposition is not complete, a glassy mass remains on cooling. It gives no ammonia when boiled with a soln. of potassium hydroxide; the nitrogen is all given off when treated with a soln. of potassium iodide or sulphide; it is decomposed by nitric acid and part is dissolved; and it is soluble in hydrochloric acid and a hot soln. of ammonium hydrophosphate. By heating Millon's base with phosphoric acid, C. F. Rammelsberg obtained a yellow compound which became grey on exposure to light, and which he regarded as *decahydrated monomercuriammonium oxymercuriammonium phosphate*, $2NHg_2OH.(NHg_2)_3PO_4.10H_2O$; but E. C. Franklin regarded it as a mixture of unchanged Millon's base with Ray's salt—*vide supra*.

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§ 38. Ammonium Amalgam

In 1808, immediately after H. Davy's announcement of the discovery of potassium and sodium, T. J. Seebeck [1] placed mercury in a cavity cut in a piece of ammonium carbonate resting on a metal plate; the latter was placed in connection with the positive pole, and the mercury with the negative pole of a battery. The mercury swelled up into a frothy mass, with the consistency of butter. The product is considered to be ammonium amalgam. Almost simultaneously, J. J. Berzelius and M. M. Pontin passed a current through a conc. aq. soln. of ammonium chloride, in such a way that the cathode dips into mercury, and obtained a similar frothy product. In place of T. J. Seebeck's ammonium carbonate, H. Davy, and J. B. Trommsdorff used ammonium chloride, and J. L. Gay Lussac and L. J. Thénard, the sulphate or phosphate, and showed that the salt itself could be connected directly with the positive pole of the battery. In any case, oxygen is evolved at the positive

pole, though with ammonium chloride, chlorine is also given off; very little gas is given off at the cathode. A convenient apparatus for the purpose is shown in Fig. 41.

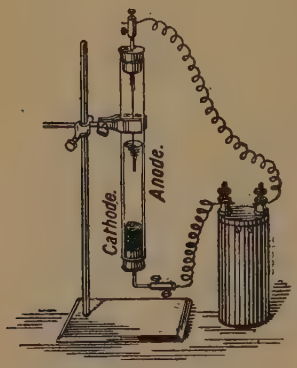

Fig. 41.—The Preparation of Ammonium Amalgam.

According to G. Michaud, the use of an amalgam of mercury with other metals—silver, gold, aluminium, bismuth, lead, etc.—in place of mercury alone, lowers the stability of the resulting ammonium amalgam, and this the more the greater the electropositive character of the metal. Thus, C. M. Wetherill found that a small amount of platinum altogether inhibits the formation of ammonium amalgam. H. Landolt, and J. Schröder employed an analogous process, and found that the greater the surface of contact with the ammonium chloride soln., the better the yield. H. Moissan electrolyzed a soln. of ammonium mercuric iodide, $(HN_4)_2HgI_4$ in liquid ammonia, or an aq. soln. of ammonium iodide, mercuric iodide and water, at −40°. S. von Laszcynsky electrolyzed a soln. of ammonium thiocyanate with a mercury cathode, using a current of 0·5 amp. and 7 volts.

H. Davy prepared ammonium amalgam by placing a little mercury containing about one per cent. of sodium potassium, or barium in moistened ammonium salt, in aq. soln., or a soln. in conc. aq. ammonia. F. S. Pfeil and H. Leffman state that if the ammonium salt is dry, no reaction occurs; but in the presence of moisture, the mercury swells up, forming the amalgam. A. Coehn found amalgams of potassium, sodium, lithium, and strontium furnished ammonium amalgam, but he was not successful with barium and magnesium amalgam. W. Kettembeil used alkali amalgams with a conc. aq. soln. of ammonium chloride. R. Böttger found sodium amalgam to be more effective than potassium amalgam. J. Proude and W. H. Wood inferred that soln. of ammonium salts in phenol, or in a soln. of pyrogallol in aq. ammonia, contained compounds of the nature of ammonium salts. C. M. Wetherill obtained ammonium amalgam by the action of sodium amalgam on a soln. of methylamine oxalate free from ammonia, and F. S. Pfeil and H. Leffman likewise with a sat. soln. of trimethylamine ammonium chloride; but not with sodium amalgam and a sat. soln. of the hydrochloride of aniline, conine, morphine, or quinine, or of rosaniline acetate. H. Moissan prepared ammonium amalgam by placing a little dry ammonium iodide or chloride in liquid ammonia, and shaking the mixture at about −35° with sodium amalgam; the product is washed with liquid ammonia to remove the ammonium and sodium iodides; and then cooled with ether to −80°. J. J. Berzelius and M. M. Pontin stated that ammonium amalgam has the consistence of butter and the colour of mercury. As shown by K. W. G. Kastner, the amalgam prepared by the electrolytic process is often crystalline. H. Davy said that the amalgam formed below 0° crystallizes in cubes, and W. R. Grove found that when cooled by a mixture of solid carbon dioxide and ether, the amalgam becomes brittle, and exhibits a dark grey, faintly lustrous fracture. J. J. Berzelius found the amalgam to be lighter than water, and J. Proude and W. H. Wood added that the sp. gr. of well-formed mercury froth is not greater than 0·730 since it floats on ether of that sp. gr. The amalgam soon decomposes into liquid mercury and a mixture of approximately 1 vol. of hydrogen and 2 vols. of ammonia. J. J. Berzelius and M. M. Pontin stated that the amalgam decomposes as soon as it is taken out of the voltaic circuit, but that which is prepared with potassium or sodium remains undecomposed a longer time because it retains a small proportion of these elements; it resists decomposition longest in an atm. of hydrogen. According to H. Davy, the decomposition in air or water is not accompanied by the absorption of oxygen or the formation of ammonium carbonate, although in dil. sulphuric acid, mercury, ammonium sulphate, and sulphur are formed; and in hydrogen chloride, ammonium chloride, mercury, and hydrogen. The action

of various impurities in the mercury on the decomposition of the amalgam, and the action of the amalgam on various salt soln., *vide infra*. L. P. Cailletet found that ammonium amalgam is decomposed by a plate of iron, platinum, or aluminium; and that agitation with sodium amalgam, in the presence of water, has a similar effect. H. Davy found that the amalgam also decomposes under fixed oil, and J. L. Gay Lussac and L. J. Thénard stated that the decomposition is accelerated by agitating the amalgam alone or with mercury, also by contact with rock oil, and still more so by contact with alcohol or ether. The decomposition of the amalgam is attended by the inflation of the mercury into a kind of froth. J. L. Gay Lussac and L. J. Thénard said that the mercury swells up to five times its original bulk: H. Davy, 8–10 times; R. Böttger, 20 times; and H. Moissan, 25 to 30 times. According to W. R. Grove, and C. F. Schönbein, the amalgam does not give off gas when cooled by a mixture of ether and solid carbon dioxide, but gas begins to be given off as the solid liquefies. H. Moissan found appreciable swelling occurs at —30°, and H. Davy said that at —29° the decomposition is as rapid as at ordinary temp. During the decomposition of the amalgam, the temp., under ordinary conditions, was found by H. Moissan to rise 5° or 6°; G. Baborovsky and V. Vojtech found that during the decomposition of the amalgam, some positive ions are given off, without photographic action. When J. J. Berzelius and M. M. Pontin communicated their discovery to H. Davy in 1808, they stated that ammonia must be an oxide like potash and soda, and that the new substance was a compound of the metallic constituent of ammonia with mercury. H. Davy applied the term *ammonium* to the supposed metallic basis of ammonia. J. L. Gay Lussac and L. J. Thénard regarded the amalgam as a triple compound of mercury, ammonium, and hydrogen, and the latter afterwards called it *l'hydrure ammoniacal de mercure*. In 1816, A. M. Ampère said:

> The difficulty in assimilating the constitution of ammoniacal to metallic salts would disappear if it be admitted that, just as cyanogen, although a compound body, exhibits all the properties of the simple bodies which are capable of acidifying hydrogen, so the combination of one volume of nitrogen and four volumes of hydrogen which is united to mercury in the amalgam discovered by T. J. Seebeck, and to chlorine in the ammonium chloride, behaves in all the compounds which it forms like the simple metallic substances.

This is virtually the present-day theory of the constitution of ammonium compounds, and was developed and extended by J. J. Berzelius. It was argued that the amalgam is a true soln. of ammonium in mercury, and that it readily decomposes into mercury, ammonia, and hydrogen when warmed above 0°, and these gases entangled with the mercury give it the appearance of a froth.

The gases obtained by the decomposition of ammonium amalgam have been analyzed by H. Davy, J. L. Gay Lussac and L. J. Thénard, H. Landolt, R. Routledge, H. Moissan, etc. The general results show that ammonia and hydrogen are present very nearly in the proportions required for the radicle NH_4. Conflicting opinions were entertained about the amalgam. For example, J. F. Daniell regarded the amalgam as a mixture of gases and mercury resulting from the cohesion of the mercury and the adhesion to it of the gases, and he likened the action to the absorption of oxygen by molten silver. W. R. Grove regarded the amalgam as a chemical compound of mercury and nitrogen inflated by hydrogen. H. Moissan followed J. L. Gay Lussac and L. J. Thénard in assuming that ammonium amalgam is ammoniacal mercury hydride because when a soln. of sodium amalgam is allowed to stand with aq. ammonia, much swelling occurs with the formation of a buttery mass which maintains itself for 2 or 3 days in the ammoniacal soln., while if sodium amalgam alone is treated with the same liquid, hydrogen is slowly evolved with no inflation of the mass. G. McP. Smith extended these experiments to potassium, lithium, barium, strontium, and calcium amalgams; he found that all formed ammonium amalgam when treated with a soln. of ammonium chloride, and also that although there is no inflation with sodium amalgam, all the others do swell. According to C. M. Wetherill, the amalgam is not an alloy of mercury and ammonium; H. Landolt

concluded that while the amalgam contains the NH_4-group in combination with mercury, it is not a veritable amalgam, because, unlike the amalgams of potassium and sodium, it does not react by double decomposition with soln. of salts of copper, silver, and iron. M. le Blanc showed that H. Landolt's failure to obtain double decompositions with ammonium amalgam and the salts of copper, silver, and iron does not disprove the metallic nature of ammonium in its amalgam, because, owing to its instability, ammonium has not the force necessary to displace metals from their compounds, but immediately decomposes on severing its union with mercury. A. Coehn further showed that when ammonium amalgam is brought in contact with a soln. of cupric sulphate at 0°, the copper is displaced from its soln.: $2(NH_4)+CuSO_4=Cu+(NH_4)_2SO_4$; he also tried to reduce metals which are not reducible by hydrogen, and he succeeded in doing so with soln. of cadmium and zinc sulphates. This, said A. Coehn, should remove the last objection to the hypothesis that ammonium has the nature of a metal. The argument, however, is not decisive. According to M. le Blanc, atomic hydrogen can displace zinc under somewhat similar conditions, but potassium, barium, etc., are not reduced in this way. Hence, if ammonium amalgam be capable of displacing these elements from their salt soln., the displacement can be the result of an exchange with ammonium in the amalgam, and not a reduction of nascent hydrogen from the decomposition of the amalgam. G. McP. Smith showed that ammonium, like the metals of the alkali and alkaline earth groups, is inversibly displacable in the form of its amalgams. C. A. Seely found that the volume of the inflated mass varied with the superimposed press., and argued that the amalgam is a soln. of gas in the mercury, and not an ammonium amalgam. A. H. Gallatin, G. W. Gunning, and W. Weyl, however, showed that the decomposition of ammonium amalgam gives hydrogen with properties of that gas *in statu nascendi*, and therefore inferred that the radicle ammonium exists in the amalgam. R. Routledge assumed that the NH_4-radicle is combined with the mercury because the gases are present in the required proportions; and because the NH_4 is apparently diffused uniformly throughout the mass. He also found that the compressibility of the inflated mass agrees fairly well with the assumption that it contains a gas and mercury, and added:

> We may admit that such a compound is originally formed, and decomposes rapidly into mercury, ammonia, and hydrogen, while the gases, becoming entangled in the mass, impart to it that remarkable turgescence, which is not, however, a property of the original compound, but merely an accidental result of its decomposition.

The swelling is not a characteristic property of the amalgam, but is a secondary phenomenon attending its decomposition, since below 0° the amalgam shows little tendency to inflation. G. Aronheim studied the electrical phenomenon attending the bubbling through the mercury of the gas from decomposing amalgam.

M. le Blanc found that when a soln. of an ammonium salt is electrolyzed with a mercury cathode, the polarization between the resulting amalgam and amalgamated zinc rises to a maximum in a few minutes, and that the maximum is nearly as high as is obtained by the similar treatment of a sodium salt. When the polarizing current is cut off, the inflated mercury cathode remains electronegative to the soln. for 10 to 20 mins. This effect is not due to the hydrogen, since the hydrogen polarization drops off almost as soon as the current is broken, while it resembles the effect obtained with amalgams of the alkali and alkaline earth salts. So that a metallic body analogous with potassium and sodium is combined with mercury in ammonium amalgam. The greater fall of potential in breaking the circuit with ammonium amalgam is due to the greater instability of the amalgam, and to its low NH_4-content. A. Coehn and K. Dannenberg measured the potential necessary for the continuous evolution of hydrogen on a mercury cathode, and found it to be 1·52 volts; with the ammonium salts at 1·24 volts, the amalgam begins to form, and this is fully analogous with the results obtained with the alkali metals. H. C. Pocklington measured the e.m.f. of a Daniell's element in which the zinc was replaced by ammonium amalgam; and

hence inferred that the amalgam contains the free radicle which rapidly decomposes into ammonia, hydrogen, and mercury. According to F. M. G. Johnson and N. T. M. Wilsmore, the e.m.f. of ammonium amalgam in a *N*-soln. of ammonium nitrate in liquid ammonia, against cadmium in a sat. soln. of cadmium nitrate, is 0·91 volt.

E. M. Rich and M. W. Travers measured the depression of the f.p. of ammonium amalgam, and inferred that it is a soln. of ammonium in mercury ; but G. McP. Smith also showed that the results also accord with the assumption that the amalgam is a soln. of a substance of the empirical composition $NH_4.Hg_n$. H. Moissan obtained no evidence of the existence of free ammonium in the reactions between ammonium chloride and lithiumammine : $2NH_4Cl+2NH_3Li=2LiCl+4NH_3+H_2$; between hydrogen sulphide and lithiumammine : $H_2S+2NH_3Li=Li_2S+2NH_3+H_2$; etc., in liquid ammonia at −100° ; nor did O. Ruff obtain any evidence of the formation of ammonium at −95° with a press. up to 60 atm. He passed a current through liquid ammonia with the electrodes surrounded by small lumps of potassium iodide, metallic potassium was liberated at the cathode, and rising to the upper layer of liquid ammonia, coloured it blue ; when ammonium iodide was substituted for potassium iodide, no blue coloration occurred. He thus doubted if such a substance as NH_4 analogous to metallic potassium can be produced, and he regarded NH_4 as a compound $H.NH_3$ analogous with $K.NH_3$, $NaNH_3$, and $Li.NH_3$. G. McP. Smith, however, argued that he has shown that alkali and alkaline earth metals exist in mercury, even in dil. soln., not in the form of single atoms, but in that of compounds of this general formula MHg_n, containing only one atom of the amalgamated metal per mol. Some of the so-called substituted ammoniums—in which one or more of the hydrogen atoms of NH_4 are replaced by one or more of the alkyl groups $CH_3.C_2H_5$, C_3H_7, . . . —are more stable than ammonium amalgam. H. N. McCoy and W. C. Moore have prepared crystalline amalgams closely resembling those of potassium and rubidium. W. Palmaer also found that the electrolysis of soln. of the substituted ammonium salts in liquid ammonia gave a blue-coloured soln. about the cathode. The blue cathode liquid has the same colour as soln. of the alkali metals in liquid ammonia, although it is less stable, for it decolorizes in a short time. Hence, it is inferred that if ammonium or a substituted ammonium could be isolated in a free state, it would exhibit metallic properties resembling the alkali metals.

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§ 39. Amalgams of the Alkali Metals

The solubility of the alkali metals in mercury increases with increasing temp. and with increasing at. wt. W. Kerp and co-workers[1] found for the percentage solubility:

	0°	25°	65°	100°
Lithium	0·04	0·07	0·11	0·13
Sodium	0·54	0·65	0·86	1·11
Potassium	0·31	0·54	1·25	2·12
Rubidium	0·92	1·37	—	—

W. Kerp and co-workers, and H. Winter also measured the solubility of sodium in mercury. T. W. Richards and R. N. G. Thomas found lithium is soluble in mercury only to the extent of 0·0036 per cent. G. McP. Smith and co-workers, and E. Maey also made observations on the solubility of lithium in mercury. The coeff. of diffusion, k, of the metals in mercury varies periodically with the at. wt. M. von Wogau found:

	Li	Na	K	Rb	Cs
$k \times 10^{-6}$	7·63	7·41	6·02	5·32	5·21

H. Davy observed that mercury and potassium readily unite at ordinary temp. with the evolution of much heat; J. Schumann said that the union is accompanied by *lebhafter Feuererscheinung*, and, according to J. L. Gay Lussac and L. J. Thénard, *sans dégagement de lumière*. V. Merz and W. Weith said that sodium reacts at a rather lower temp., and more vigorously than potassium; J. L. Gay Lussac and L. J. Thénard said that the reaction between sodium and mercury is attended by *un grand dégagement de chaleur et de lumière*. G. S. Sérullas, indeed, stated that when a piece of sodium is projected on mercury, it may be thrown out of the vessel with an explosion owing to the great development of heat. The rapid gyratory movement which occurs when a piece of potassium or sodium is placed on mercury, depends on the absorption and decomposition of atm. moisture by the alkali metal; and the liberation of hydrogen gives rise to the motion; if the experiment be made in dry air, the amalgamation is tranquil—3·24 c.c. of gas per gram of sodium is given off during the formation of sodium amalgam—if the sodium used be purified in vacuo, L. Kahlenberg and D. Klein obtained no hydrogen.

The amalgams can be prepared by mixing the component metals. R. Böttger rubbed the two metals in a dry mortar fitted with a cover, and preserved the product under a layer of naphtha. G. McP. Smith added 15 grms. of sodium in small pieces at a time at ordinary temp. to one kgrm. of mercury; the temp. rose to 150°. The amalgam is then kneaded under water, and dried with filter paper. K. Bornemann and G. von Rauschenplat, C. Löwig, J. Schumann, W. Kerp and co-workers, H. Winter, A. Guntz and J. Férée, and M. Rosenfeld used a similar process. It is difficult to prepare directly amalgams of the alkali metals with a definite composition because, as M. Berthelot, and N. S. Kurnakoff pointed out, a part of the sodium is oxidized; in consequence, H. G. Byers, E. Jänecke, and M. Reuter worked in an atm. of hydrogen, and E. Vanstone in an atm. of carbon dioxide; J. Schumann melted the alkali metal under petroleum, and added the mercury to the metal; the temp. rose to the ignition point of the oil. Hence, O. Mühlhäuser added the mercury in a very thin stream. T. W. Richards and J. B. Conant prepared sodium amalgams by electrolysis:

A sat. soln. of pure sodium carbonate (four times recrystallized and centrifuged) was electrolyzed in a cell consisting of an ample mercury cathode and an anode of platinum foil; a wide-mouthed half-litre bottle served as the container. After passing a current of 4 ampères for a few hours, the amalgam became pasty and the process was stopped. The electrolyte was poured off as completely as possible and the amalgam was thoroughly agitated with 4 or 5 portions of distilled water and subsequently with 2 portions of alcohol. It was transferred to a small flask which was evacuated and heated for some minutes. Having been thus dried, it was placed while still hot in a desiccator, where it remained until it was diluted, and filtered through a capillary tube in order to eliminate the film of hydroxide.

A. Schüller, E. Maey, A. C. Vournasos, P. T. Muller, N. S. Kurnakoff, H. N. Draper, G. McP. Smith, G. N. Lewis and C. A. Kraus, L. Schüz and E. Vanstone mixed the metals under a layer of paraffin or petroleum oil; and M. Reuter under a layer of xylol. The hydro-carbon is difficult to remove completely from the product. N. S. Kurnakoff and G. J. Zukowsky made cæsium amalgam by the direct union of the elements. E. Maey, G. McP. Smith, and G. J. Zukowsky also made lithium amalgam by the direct union of the elements. A. D. Hirschfelder and M. C. Hart prepared sodium amalgam in the form of fine flocculi by pouring hot liquid amalgam into a jar of xylene or kerosene agitated by an electrical stirrer. The amalgam was allowed to settle, and dried in a current of air.

There is a reversible displacement of the alkali metals in amalgams and in aq. soln. of their salts. For example, sodium amalgam in a soln. of potassium hydroxide was found by J. Schumann, G. McP. Smith, and W. Kettembeil, to form potassium amalgam. G. Fernekes, and G. McP. Smith obtained similar results with soln. of the alkali chlorides. The latter also found that potassium amalgam forms sodium amalgam in a soln. of sodium hydroxide or sodium chloride. Similarly also with lithium amalgam. P. Schorigin obtained sodium amalgam by the action of sodium ethide, NaC_2H_5, on mercury: $2C_2H_5Na+2Hg=2HgNa+C_2H_4+C_2H_6$. The reaction between mercuric diethyl and sodium does not proceed so smoothly.

The alkali metals are not always conveniently available for preparing amalgams, and in that case electrolytic methods are available. M. Reuter pointed out that judging from the records of these methods, however, the products nearly always have a low percentage proportion of the alkali metal; conc. amalgams have not been obtained. J. J. Berzelius and M. M. Pontin prepared potassium amalgam by placing mercury in a cup covered with a conc. soln. of potassium hydroxide; the mercury serves as negative electrode, a metal wire dipping in the soln. as positive electrode. On electrolysis, potassium amalgam is formed. J. Schumann, G. McP. Smith and H. C. Bennett, T. W. Richards and E. Müller, and R. Lüpke employed a similar process also involving the use of the mercury cathode. W. Kerp, G. Bird, G. McP. Smith and H. C. Bennett, and E. S. Shepherd, electrolyzed a soln. of potassium or sodium chloride with a mercury cathode; and S. von Laszcynsky, a soln. of potassium or sodium thiocyanate. W. Kerp and co-workers, and G. McP. Smith and H. C. Bennett made rubidium amalgam, and the latter also cæsium and lithium amalgam by the electrolysis of soln. of the chlorides with mercury as cathode. G. McP. Smith and J. R. Withrow electrolyzed soln. of lithium acetate or sulphate using a mercury cathode. A. Guntz and J. Férée, and K. Bornemann and G. von Rauschenplat made lithium amalgam by the electrolysis of soln. of the chlorides. E. Mitscherlich used a soln. of lithium hydroxide as electrolyte. The electrolytic method was modified by O. Arlt who allowed a stream of mercury to fall through a soln. of a salt of the alkali metal, and kept a protective layer of carbon disulphide or chloroform between the mercury layer and the electrolyte during the passage of the current. The method was employed by W. Nernst, W. Kerp and W. Böttger, J. R. Withrow, and P. M. Giesy and J. R. Withrow, E. C. Bain and J. R. Withrow. E. S. Shepherd suspended a mercury cathode in a porous cup at the surface of the sodium salt soln. being electrolysed; this avoided the insulating action of the specifically lighter amalgam which accumulates at the surface of the mercury. The method was employed by

G. McP. Smith and J. R. Withrow, S. B. Frank and J. R. Withrow, and P. M. Giesy and J. R. Withrow. S. B. Frank and J. R. Withrow prepared solid alkali amalgams by electrolysis.

The f.p. curve of the lithium amalgams, by G. J. Zukowsky,[2] is shown in Fig. 42; there is a eutectic at 162° between Li_3Hg and lithium, and the eutectic has 97 atomic per cent. of lithium; there is a bend in the curve at 275° and 83·6 atomic per cent. of lithium corresponding with the transition of Li_3Hg into what is possibly Li_3Hg_2 or Li_2Hg; and at 406° and 65·3 atomic per cent. of lithium, this begins to decompose, forming LiHg. There is a maximum—dystectic—point at 600·5° with 50 atomic per cent. of lithium corresponding with the compound LiHg. The transformations at 338° and 30·1 atomic per cent. of lithium, and at 232° and 17·6 atomic per cent. of lithium respectively correspond with the formation of compounds $LiHg_2$ and $LiHg_3$. There is a second eutectic at −42° with less than one per cent. of lithium. According to E. Maey, the sp. vol. curve shows singular points corresponding with **lithium hexamercuride,** $LiHg_6$, and with **lithium pentamercuride,** $LiHg_5$. A. Guntz and J. Férée prepared the pentamercuride by the electrolysis of soln. of lithium

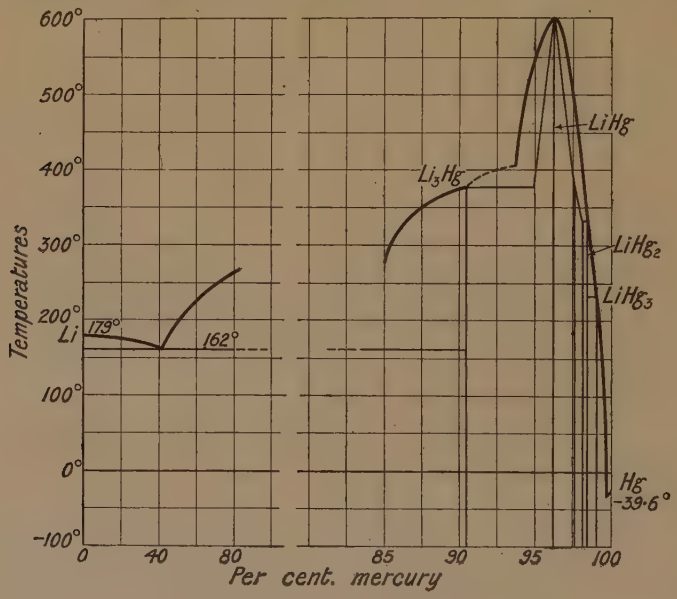

Fig. 42.—Freezing-point Curve of Lithium Amalgams.

chloride with a mercury cathode. E. Maey said that it forms six-sided, needle-like crystals. W. Kerp and co-workers found that the crystals melt over 100°, at 100° the crystals are mixed with liquid, and the two form a mobile mush at 125°, and all is melted at 165°. G. J. Zukowsky obtained needle-like crystals corresponding with **lithium trimercuride,** $LiHg_3$; E. Maey obtained evidence of this compound on the sp. vol. curve; and G. McP. Smith and H. C. Bennett isolated the crystals by centrifuging the mass. G. J. Zukowsky obtained a mass with needle-like crystals of **lithium dimerchuride,** $LiHg_2$; and cubic crystals of **lithium monomercuride,** LiHg, of hardness 2 to 3. E. Maey obtained evidence of this compound on the sp. vol. curve. G. J. Zukowsky obtained a mass with needle-like crystals thought to be **lithium hemimercuride,** Li_2Hg, or **lithium ditritamercuride,** Li_3Hg_2; similarly also of **lithium tritamercuride,** Li_3Hg. Evidence of this latter compound on the sp. vol. curve was obtained by E. Maey. G. McP. Smith obtained crystals by filtering the electrolytically prepared amalgam through leather, and afterwards treating the product in a centrifuge. F. H. Newman studied the spectra of alkali amalgams.

The f.p. curve of the sodium amalgams is shown in Fig. 43. There is a maximum at 360° corresponding with $NaHg_2$; and A. Schüller interprets the rest of the curve as representing the formation of $NaHg_4$ at 159°; $Na_{12}Hg_{13}$ at 227°; of NaHg at 219°; of Na_3Hg_2 at 125°; of Na_5Hg_2 at 62°; and of Na_3Hg at 34°. The f.p. curve of sodium and mercury was also studied by M. Berthelot, W. Kerp and co-workers, V. Merz and W. Weith, K. Bornemann, N. S. Kurnakoff, A. Gorboff, C. H. Desch, G. Tammann, P. I. Bachmetjeff and J. V. Wsharoff, E. Vanstone, E. Maey, D. Mazzotto, P. T. Muller, and L. Schüz. M. Berthelot assumed the existence of **sodium octomercuride,** $NaHg_8$; and A. Guntz and J. Férée claim to have obtained it in crystals by cooling a 0·57 per cent. sodium amalgam to −19°, and separating the excess of mercury; and A. Joannis, by the slow action of mercury on a soln. of sodammonium in liquid ammonia. H. Winter, N. S. Kurnakoff, E. Maey, and G. Tammann studied **sodium hexamercuride,** $NaHg_6$, K. Kraut and O. Popp prepared it by the action of a soln. of sodium hydroxide or carbonate on 3 per cent. sodium amalgam, and squeezing out the excess of mercury; W. Kerp and co-workers by crystallization from sodium amalgam sat. at 75°, and cooled to 25°; and A. Guntz and J. Férée by slowly cooling a soln. of sodium in mercury, and squeezing out the excess of mercury. The needle-like crystals were stated by the latter to belong to the cubic system. W. Kerp and co-workers said that they form a mush at 39°, and are all melted at 58°; and form **sodium pentamercuride,** $NaHg_5$, between 40° and 42°. G. P. Grimaldi believed that K. Kraut and O. Popp's Na_2Hg_{12} is really the pentamercuride. W. Kerp's analyses of the compound, prepared at temp. ranging from 0° to 99·8°, have the mean value 2·13 per cent. Na. G. McP. Smith and H. C. Bennett's analyses varied from 2·12 to 2·28 per cent. Na. It is the richest solid sodium amalgam. W. Kerp obtained it from the amalgam at a temp. over 25°; W. Kerp, W. Böttger, and H. Winter, above 100°; G. P. Grimaldi, by centrifuging a 1·4 per cent. sodium amalgam; and A. Guntz and J. Férée, by melting the hexamercuride and adding a rather richer amalgam; then heating the whole to 200°; cooling to 140°, and decanting off the excess of mercury. The prismatic crystals were found by G. P. Grimaldi to melt at 145°, but, according to W. Kerp, fusion begins at about 105°, a thick mush is formed at 19°, and all is melted at 138°–139°, and it is not stable above 105°. G. P. Grimaldi measured the electrical resistance, and W. Kerp, the solubility in 100 parts of mercury:

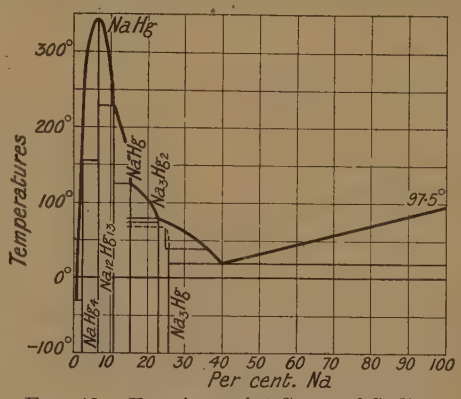

Fig. 43.—Freezing-point Curve of Sodium Amalgams.

	0°	25°	40°	56·7°	81°	99·8°
$NaHg_5$ per cent.	24·33	28·79	32·25	35·58	41·14	49·46

W. Kerp and co-workers obtained crystals corresponding with **sodium tetramercuride,** $NaHg_4$, from sodium amalgam over 180°; A. Guntz and J. Férée, by squeezing the hexa- or penta-mercuride at 200 to 1200 kgrms. per sq. cm.; and A. Schüller, by melting an amalgam with 20 at. per cent. of sodium over 220°, and slowly cooling while it is being stirred. E. Vanstone obtained long prismatic crystals. W. Kerp doubted the existence of this as a chemical individual. M. Berthelot, and K. Bornemann also studied this compound. In his study of the f.p. curve, N. S. Kurnakoff obtained evidence of a compound Hg_nNa, where n is less than 5 and greater than 2, and by analogy with the corresponding potassium

compound he assumed it to be **sodium trimercuride,** $NaHg_3$. A. Schüller obtained crystals of **sodium dimercuride,** $NaHg_2$, by melting a 33·3 at. per cent. sodium amalgam above 360°. E. Jänecke gave 350° for the m.p. This compound has been studied by N. S. Kurnakoff, G. Tammann, E. Maey, M. Berthelot, K. Bornemann, and P. T. Muller. There are four doubtful compounds Hg_nNa with n between 1 and 2. N. S. Kurnakoff obtained evidence of one being formed by the decomposition of the monomercuride at 209·7°; E. Maey and M. Berthelot, Na_4Hg_7; E. Vanstone, Na_7Hg; and K. Bornemann and A. Schüller, $Na_{12}Hg_{13}$. N. S. Kurnakoff and A. Schüller obtained evidence of the existence of **sodium monomercuride,** NaHg, on the f.p. curve. E. Vanstone, M. Berthelot and E. Maey studied its properties. E. Jänecke found the prismatic crystals melted at 217°; and N. S. Kurnakoff, that they decomposed at about 209·7°. E. Vanstone, K. Bornemann, and A. Schüller obtained crystals of **trisodium dimercuride,** Na_3Hg_2. H. von Wartenberg found that Na_3Hg is stable in the vapour phase between 380° and 444°. N. S. Kurnakoff, and E. Maey also obtained evidence of the existence of a compound Na_nHg, when n is equal to or less than 2·5. A. Schüller, and K. Bornemann obtained evidence of **sodium dipentitamercuride,** Na_5Hg_2, but E. Vanstone doubted if such a compound really exists. E. de Souza obtained **sodium tritamercuride,** Na_3Hg, by heating sodium amalgam with an excess of mercury to 400°. E. Vanstone, E. Maey, K. Bornemann, and G. Tammann studied this product.

E. Jänecke obtained the f.p. curve of potassium amalgams, Fig. 44, and found a maximum at 279° corresponding with KHg_3, and the rest of the curve is interpreted to show the formation of KgH at 178°; HgK_3 or K_9Hg_3 at 204°; K_2Hg_9 at 173°; and KHg_9 or KHg_{10} at 70°. The f.p. curve has also been studied by M. Berthelot, V. Merz and D. Mazzotto, W. Weith, G. Tammann, N. S. Kurnakoff; W. Kerp, W. Böttger, and H. Winter, K. Bornemann, P. Müller, and E. Maey. Crystals of what A. Guntz and J. Férée regarded as **potassium octodecamercuride,** KHg_{18}, were obtained by cooling an amalgam of the two metals to —19°. W. Kerp, W. Böttger, and H. Winter obtained **potassium tetradecamercuride,** KHg_{14}, from an amalgam by press. between —2° and —12°. E. Jänecke, K. Bornemann, and G. Tammann obtained evidence of the existence of a compound, **potassium enneamercuride,** KHg_9, on the f.p. curve, and A. Joannis obtained it by the action of mercury on a soln. of potassammonium in liquid ammonia. There is some uncertainty about the composition of this product.

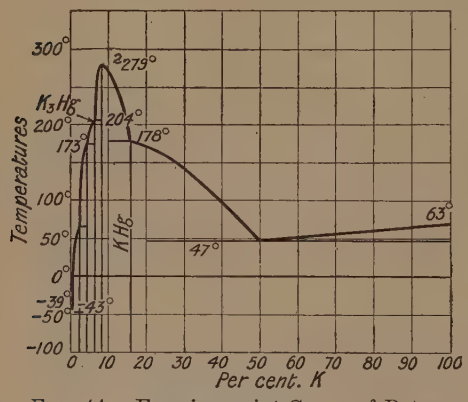

FIG. 44.—Freezing-point Curve of Potassium Amalgams.

N. S. Kurnakoff showed that the enneamercuride may be KHg_{10}; and K. Kraut and O. Popp, W. Kerp and co-workers have reported the preparation of *potassium decamercuride*, KHg_{10}; J. H. Croockewit by melting together the components; G. P. Grimaldi by melting and cooling an amalgam with 1·77 per cent. of potassium; and A. Guntz and J. Férée, by compressing the dodecamercuride at 200 kgrms. per sq. cm. It melts about 60°. G. P. Grimaldi measured the electrical resistance. E. Maey reported *potassium henadecamercuride*, KHg_{11}, and J. H. Croockewit, *potassium dodecamercuride*, KHg_{12}, by melting together the constituents; by K. Kraut and O. Popp, by the action of potassium hydroxide or carbonate, not acetate or chloride, on 3 per cent. sodium amalgam; by A. Guntz and J. Férée, by warming the octodecamercuride with potassium; W. Kerp and co-workers, by pressing the tetradecamercuride; and W. Kerp, by cooling for some days at 0° the amalgam prepared electrolytically. The crystals of the alleged dodecamercuride belong to the cubic system; they are stable between 0° and 70°; and they melt and decompose

at 75°. Various analyses have been made by G. McP. Smith and H. C. Bennett, K. Kraut and O. Popp, W. Kerp and co-workers, etc. M. Berthelot claimed to have shown the existence of *potassium octomercuride*, KHg_8; E. Divers, of *potassium heptamercuride*, KHg_7; M. Berthelot, and N. S. Kurnakoff, of *potassium hexamercuride*, KHg_6; E Maey, and N. S. Kurnakoff, of *potassium pentamercuride*, KHg_5. K. Bornemann, and E. Jänecke obtained evidence on the f.p. curve of what was regarded as *potassium hemienneamercuride*, K_2Hg_9, in six-sided plates melting at 173°, but N. S. Kurnakoff assumed that the penta or hexa- mercuride is here in question. E. Maey, and M. Berthelot discussed the existence of potassium tetramercuride, KHg_4.

K. Bornemann, N. S. Kurnakoff, E. Maey, and E. Jänecke obtained evidence on the f.p. curve of the existence of crystals of **potassium trimercuride,** KHg_3, or K_3Hg_9. The latter gave 204° for the m.p. E. Maey, G. Tammann, K. Bornemann, and E. Jänecke likewise obtained evidence of **potassium dimercuride,** KHg_2; and G. Tammann, E. Maey, and E. Jänecke of **potassium monomercuride,** KHg, melting at 178°. E. de Souza prepared a crystalline mass of **potassium hemimercuride,** K_2Hg, by heating potassium amalgam with an excess of mercury to 440°. F. C. Accum, W. Böttger, and G. McP. Smith prepared mixed sodium and potassium amalgam; and E. Jänecke, by using eq. proportions of the constituent elements, obtained **sodium potassium mercuride,** $NaKHg_2$, melting at 188°.

N. S. Kurnakoff found the f.p. curve of rubidium amalgam has a maximum at 136·5° corresponding with **rubidium hexamercuride,** $RbHg_6$, and there are indications of **rubidium tetramercuride,** $RbHg_4$, and **rubidium dimercuride,** $RbHg_2$. W. Kerp and co-workers, and G. McP. Smith and H. C. Bennett also studied these amalgams. G. McP. Smith and H. C. Bennett also claimed to have formed silvery cubic crystals of **rubidium dodecamercuride,** KHg_{12}, by centrifuging the amalgam. It melts with decomposition below 0°. The f.p. curve for cæsium amalgams has been studied by N. S. Kurnakoff and G. J. Zukowsky, A. Gorboff, C. H. Desch, K. Bornemann, and G. McP. Smith and H. C. Bennett. There is a maximum at 208·2° corresponding with **cæsium dimercuride,** $CsHg_2$, Fig. 45; one at 163·5° corresponding with **cæsium tetramercuride,** $CsHg_4$, or $CsHg_3$; and one at 157·7° corresponding with **cæsium hexamercuride,** $CsHg_6$; and at about 13° **cæsium decamercuride,** $CsHg_{10}$, is formed; there are also indications of the formation of **cæsium hemimercuride,** Cs_2Hg, and **cæsium monomercuride,** CsHg. The mercurides of the type MHg_2, MHg_4, and MHg_6 thus appear to be common to the four alkali metals M=Na, K, Rb, and Cs. N. S. Kurnakoff also thinks that similar cadmides are formed—MCd_2, MCd_4, and MCd_6. G. McP. Smith and H. C. Bennett claimed to have made crystals of **cæsium dodecamercuride,** $CsHg_{12}$, by centrifuging the amalgam.

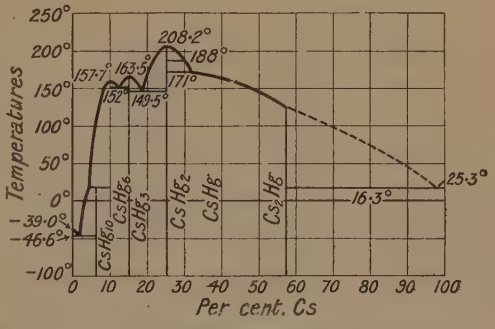

FIG. 45.—Freezing-point Curve of Cæsium Amalgams.

The physical properties of the alkali amalgams.—Lithium amalgam with 0·0597 per cent. of lithium was found by W. Ramsay [3] to give needle-like crystals which melted in air. W. A. Lampadius found that sodium amalgam with 3·2 per cent. of sodium has a crystalline fracture and can be filed to a powder; and a 2·44 per cent. amalgam is solid. L. Schüz found that amalgams with 3–10 per cent. of sodium are hard brittle solids; and K. Kraut and O. Popp found that the 1·9 per cent. amalgam has needle-like crystals. R. Böttger found a 1·6 per cent. amalgam forms a pasty mass at 21°; likewise also a 1·23 per cent. amalgam; a one per cent. amalgam also has a liquid and a solid portion; while J. L. Gay Lussac and L. J. Thénard found a 0·78 per cent. amalgam is liquid. According to A. Battelli,

amalgams with the atomic ratio between Na : Hg=1 : 495 and 1 : 15 are liquid, those with more sodium are solid. H. Davy found a 3·2 per cent. potassium amalgam is hard and brittle, a 1·4 per cent. amalgam is solid, and a more dil. amalgam is liquid. J. L. Gay Lussac and L. J. Thénard found that amalgams with over 1 per cent. of potassium are solid, and liquid with less than 0·7 per cent. of potassium. R. Böttger found that the amalgam is solid, and one with 0·55 per cent. potassium is friable and partly crystalline, and that with 0·5 per cent. of potassium, the amalgam is viscid. The m.p. curves for the alkali amalgams are indicated in Figs. 41 to 44.

The solid amalgams of the alkali metals are lighter than mercury or dil. liquid amalgams, and therefore float on the surface of these liquids. E. Maey's determinations of the sp. vol. of the alkali amalgams furnish the following values for their **specific gravity.** The results show that the sp. gr. becomes progressively less as the conc. of the alkali metal increases.

Per cent. Li	0·0301	0·503	2·166	8·39	11.03	19·58
Sp. gr.	13·500	13·135	10·925	6.050	5·030	2·945
Per cent. Na	0·103	0·597	2·631	5·08	11·50	39·50
Sp. gr.	13·448	12·965	11·701	10·101	6·743	2·420
Per cent. K	0·184	0.950	2·82	5·14	12·87	18·61
Sp. gr.	13·371	12·908	11·564	9·950	6·406	4·737

Measurements were also made by J. R. Withrow and co-workers, E. S. Shepherd, J. Whiting, W. Kerp, etc. E. Vanstone sought a relation between the mol. vol. of the sodium amalgams and valency. G. McP. Smith measured the speed of **diffusion** and **surface tension** of alkali amalgams. E. Maey found the **coefficient of cubical expansion** of liquid sodium amalgams between 10° and 20° to be $\alpha=0{\cdot}000181+0{\cdot}000127w$, where w represents the per cent. of alkali metal; for liquid potassium amalgams, $\alpha=0{\cdot}000181+0{\cdot}000065w$; and for lithium amalgams, $\alpha=0{\cdot}000181+0{\cdot}000017w$. According to L. Schüz, the **specific heat** of an amalgam with 10 per cent. of sodium between 62·2° and 63·2° is 0·06013—0·05930; between —21·65° and —21·37°, 0·05387 to 0·05396; between —39·91° and —39·43°, 0·05113 to 0·05076; and between —77·37 and —77·04°, 0·05167 to 0·05213. Likewise for a 3 per cent. sodium amalgam, between —20·52° and —20·76°, 0·03788 to 0·03818; and between —79·28° and —79·59°, 0·04050 to 0·04230. G. N. Lewis and C. A. Kraus found the **heat of solution** of one eq. of sodium in a large quantity of 0·206 per cent. sodium amalgam to be 19·79 Cals. M. Berthelot gave 16·2 Cals. for the **heat of formation** of $NaHg_2$ from liquid mercury; 11·4 Cals. for NaHg; 13 Cals. for Na_3Hg; H. von Wartenberg gave 13,000 cals. ±10 per cent. M. Berthelot found for the heat of formation of KHg, 12·1 Cals.; for KHg_2, 19·8 Cals.; and for KHg_3, 29·1 Cals. M. Berthelot calculated from the heat developed by the action of hydrochloric acid, the heat of combination per 2 eq. of potassium for amalgams:

K per cent.	0·337	0·65	1·34	1·85	2·00	3·40	8·01	11·85
Cals.	26·2	30·2	33·7	34·2	34·8	29·7	20·6	15·3
	Liquid	Mush		Solid				

Similarly, for sodium amalgams:

Na per cent.	0·45	0·85	1·88	2·47	4·80	5·45	10·0
Cals.	18·8	19·8	21·1	21·1	18·0	17·8	10·3
	Liquid	Mush	Solid				

The **vapour pressures** of the metal-amalgams have been measured by W. Ramsay,[4] and the conclusion drawn that the metals are monatomic when dissolved in mercury. H. von Wartenberg failed to get satisfactory measurements of the vap. press. of the compound Na_3Hg. He assumed that a compound exists

in the state of vapour at about 500°, but O. Neumann's vap. press. observations do not support this hypothesis. C. T. Heycock and F. H. Neville have measured the **freezing point** of amalgams and have drawn similar conclusions. G. Tammann likewise inferred that the metals are dissolved as simple monatomic mols. A. Larsen inferred that the degree of ionization of the dissolved metal increases with decreasing conc. and rising temp. G. Meyer showed that the e.m.f. E of cells with amalgam electrodes containing a different proportion C_1 and C_2 of metal, and a salt soln. used as electrolyte, is given by $nE=RT \log (C_1/C_2)$, where R is the gas constant, T the absolute temp., and n the number of unit charges carried by a mol. of the metal. If the metal is monatomic, n represents the valency of the metal; and if the metal has a polyatomic mol., then dividing n by the valency, there remains n' the number of atoms in the mol. The value of n/n' was found by A. Schöller, T. W. Richards and G. N. Lewis, and H. Fay and E. North to be equal to unity with a number of amalgams. F. Haber showed that the conclusion is not justified unless it can be shown that the dissolved metals are not present as compounds MHg_n. K. Bornemann also showed that these deductions apply only with solutes which have no inclination to form compounds with the solvent. G. McP. Smith also showed that the f.p., and the vap. press. methods prove only that the solute is present either in single atoms or as mols. MHg_n. According to V. Merz and W. Weith, L. Schüz, and G. McP. Smith, the general results show that *in all probability amalgams are soln. of compounds of the dissolved metal with certain definite proportions of the solvent mercury in an excess of mercury.* E. Beckmann and O. Liesche found the effect of the alkali metals on the b.p. of mercury corresponded with the formation of $NaHg_{5 \text{ or } 6}$, and of $KHg_{12,\ 13,\ \text{or}\ 14}$ at these temp.

L. Arons[5] found that when sodium amalgam is used as electrode for the **amalgam arc-lamp** the electrode tension is smaller than with mercury, and the sodium lines are strongest in the spectrum at the cathode. Potassium amalgam behaves similarly, but the spectrum rarely shows potassium lines. The **photo-electric effect** with potassium amalgams has been studied by R. Pohl and P. Pringsheim. F. H. Newman studied the spark spectra of the alkali amalgams.

The **electric conductivity** of sodium amalgam shows no discontinuity between 107° and 133°, but is rapidly lowered by alloying sodium with the mercury; there is a break in the curve at the eutectic point, and another when 22·1 atomic per cent. of mercury is present. This does not coincide with the thermal diagram, where the curve passes through a flat minimum. According to R. C. Rogers,[6] there is a sharp bend in the curve showing the relation between the percentage change of electrical resistance and the composition at the eutectic point and 5·9 atomic per cent. of sodium, but the curve is smooth if the specific resistance be plotted against the atomic composition. K. Bornemann and G. von Rauschenplat measured the sp. resistance R and the sp. conductivity of lithium, and sodium amalgams of different conc. and a different temp. and found

		50°	100°	150°	200°	250°	300°
0·003 per cent. Li	R	0·9882	1·0380	1·0921	1·1540	1·2218	$1·2954 \times 10^4$
	λ	1·0117	0·9634	0·9157	0·8665	0·8185	$0·7720 \times 10^{-4}$
0·043 per cent. Li	R	0·9750	1·0150	1·0700	1·1270	1·1920	$1·2590 \times 10^4$
	λ	1·0257	0·9852	0·9346	0·8873	0·8389	$0·7943 \times 10^{-4}$

they also computed the temp. coeff. of the resistance. Similarly for 0·11 per cent. sodium amalgam:

R . . .	0·9976	1·0274	1·1020	1·1656	1·2360	$1·3142 \times 10^4$
λ . . .	1·0024	0·9733	0·9074	0·8579	0·8091	$0·7609 \times 10^{-4}$

G. P. Grimaldi, P. Müller, and A. Battelli measured the electrical conductivity of sodium and potassium amalgams at different conc. and temp.

A. Coehn and A. Lotz[7] found that potassium and sodium amalgams in vacuo are negatively charged with respect to glass. According to A. Oberbeck and J. Edler,

the **electromotive force** of the amalgams towards mercury is in general equal to that of the metals themselves. G. McP. Smith found that the electrochemical series of the alkali amalgams in an eq. soln. of a mercury salt is: +Li, K, Rb, Cs, Na-; and he measured the e.m.f. of different alkali amalgams against potassium amalgam. M. Reuter measured the potential of potassium amalgam against $Hg(Hg_2O)$, *N*.KOH in a methyl alcohol soln. of lithium chloride. F. Haber and M. Sack, and W. Kettembeil made analogous observations with sodium amalgams. G. N. Lewis and C. A. Kraus measured the e.m.f. of sodium amalgams and sodium. E. Branly measured the e.m.f. of sodium amalgam against mercurous sulphate and carbon. T. W. Richards and J. B. Conant measured the e.m.f. of conc. cells of sodium amalgams at 15° and 25°, and the deviations from the simple concentration-law were greater than with any other amalgam yet studied. The heats of transfer of sodium from one amalgam to another were calculated. F. Glazer, measured the e.m.f. of the cell $K_{amalgam} \mid KCl \mid Cl$; J. Regnauld, of potassium amalgam in a soln. of potassium iodide with some iodine, bromine, or chloride against carbon in a soln. of potassium iodide; E. Beetz, of $K_{amalgam} \mid KOH \mid KMnO_4 \mid MnO_2$; C. Hockin and H. A. Taylor, the e.m.f. of potassium or sodium amalgam against amalgamated zinc in a conc. soln. of zinc sulphate, and under molten paraffin; C. Wheatstone, of $K_{amalgam} \mid ZnSO_4$ soln. against $CuSO_4$ soln. and Cu or dil. H_2SO_4 and PbO_2, or dil. H_2SO_4 and MnO_2; M. le Blanc, of $K_{amalgam}$ in a *N*-soln. of sodium chloride against zinc amalgam, and similarly also with sodium amalgam in *N*-NaCl. Other observations were made by G. Meyer, H. P. Cady, A. Schöller, etc. T. W. Richards and K. N. G. Thomas measured the e.m.f. of lithium amalgam against pyridine soln. of lithium chloride; and G. N. Lewis and F. G. Keyes, in propylamine sat. with lithium iodide, as well as against a normal calomel electrode. B. S. Neuhausen measured the e.m.f. of cells made with sodium amalgam, soln. of sodium chloride, and the calomel electrode. T. W. Richards and G. S. Forbes did not find an indifferent electrolyte for cells with sodium-amalgam electrodes. G. N. Lewis, E. Q. Adams, and E. H. Lanman found the transport of the metal is not related to an increase or decrease in the resistance of the mercury produced by the dissolution of the metal. G. Mayr stated that the solute metal during electrolysis is transported towards the anode, and that with respect to the transport, there is no appreciable distinction. (i) between metals, like thallium, which form compounds with the mercury, and those, like zinc, which dissolve in the mercury; and between metals, like sodium and potassium, which increase the resistance of the mercury, and those, like zinc, which diminish the resistance. S. B. Frank and J. R. Withrow studied the **electro-endosmosis** of the alkali metal amalgams. F. Skaupy considered the effect of the hydrargyration of the mercury ions on the transport number of liquid amalgams.

Some chemical properties of the alkali amalgams.—H. Davy [8] found that sodium and potassium amalgams readily change when exposed to the **air**; M. Berthelot showed that a superficial film of alkali hydroxide or carbonate is formed; and L. Schüz found a 9·58 per cent. potassium amalgam oxidizes in a few minutes. G. McP. Smith found lithium amalgam is less stable in air than either sodium or potassium amalgam. G. S. Johnson found that liquid sodium or potassium amalgam retains an untarnished lustre in dry **oxygen** at ordinary temp. and at press. ranging from 0·05 mm. to a little over 760 mm. The amalgam kindled when heated below redness in dry oxygen and burned with explosive violence. G. McP. Smith said that with potassium amalgam, a dark film of potassium suboxide mixed with mercury is first formed, and he found that while the purified amalgam reacts slowly with water, that which is partially oxidized reacts turbulently. H. Davy found that **water** slowly decomposes alkali amalgam, furnishing hydrogen, mercury, and potassium hydroxide; dil. acids act similarly, producing the corresponding alkali sat. N. S. Kurnakoff and G. J. Zukowsky found that the last three of cæsium are retained very tenaciously by cæsium amalgam in the presence of water; and G. McP. Smith observed that lithium amalgam is decomposed by

water more vigorously than potassium or sodium amalgam. E. Müller and A. Riedel determined the rate of decomposition of water by 0·2 per cent. sodium amalgam in the presence of metallic and other substances. The amalgam (80 grms.) was rapidly stirred with 50 c.c. of water and a piece of the metal in question, and the hydrogen collected and measured. The experiments were carried out with ferro-molybdenum, cast iron, wrought iron, iron carbide, silicon, ferro-silicon, ferro-vanadium, ferro-tungsten, chromium, platinum, palladium, iridium, nickel, cobalt, manganese, tantalum, graphite, and ferric oxide. It is shown that the iron alloys of molybdenum, vanadium, tungsten, and chromium have a very strong catalytic action on the process. This action depends on the increase in the surface of the amalgam due to the soln., and subsequent separation of the metals. There is a possible application of this action to the manufacture of sodium hydroxide by the mercury electrode process. O. W. Richardson measured the emission of electrons when potassium-sodium alloys are dropped through water vapour at a low press. K. Kraut and O. Popp obtained KHg_{12} by the action of a 3 per cent. sodium amalgam on an aq. soln. of **potassium hydroxide, or carbonate.** F. Haber and M. Sack observed that when an amalgam with more than 15 per cent. of sodium is dipped in water or a soln. of **sodium hydroxide,** it first becomes spongy, and then furnishes hydrogen, while amalgams poor in sodium give off hydrogen from the beginning. W. Kerp added that the decomposition of sodium amalgam by water or a soln. of a sodium salt progresses very slowly, with a soln. of commercial sodium hydroxide turbulently, and with a soln. of purified sodium hydroxide slowly. G. Fernekes found that with N- or $\frac{1}{10}N$-soln. of **sodium aluminate, hydrocarbonate, hydrophosphate, sulphite,** or the ordinary hydroxide, the action accompanied by the evolution of hydrogen is more violent than with water; and less violent with soln. of **sodium chloride, bromide, iodide, sulphate, borate, pyrophosphate, acetate,** or the purified hydroxide. J. Schumann found that a one per cent. sodium amalgam decomposes most of the **metal chlorides** and forms with them the corresponding amalgam, and likewise also by triturating the alkali amalgam with the powdered **metal.** According to N. Bunge, **mercuric** or **auric chloride** and the **silver halides** are easily reduced by sodium amalgam; silver chloride is not reduced under petroleum; an aq. soln. of **ferric chloride** is reduced partly to ferrous chloride, partly to the metal, and if sufficient amalgam is present, iron-amalgam is formed; an ethereal soln. of ferric chloride is changed but slowly; and a dil. hydrochloric acid soln. of **chromic chloride** furnishes a green liquid and chromium amalgam. O. W. Richardson studied the emission of electrons when potassium-sodium alloys are dropped through **carbonyl chloride, chlorine,** and **hydrogen chloride** at a low press.

R. Böttger, H. G. Byers, and G. McP. Smith found that sodium amalgam reacts with **salts of the alkaline earths or the heavy metals** in the presence of a little water, forming the corresponding amalgams. Similar results were obtained with potassium salts, and generally, potassium amalgam reacts more strongly than does sodium amalgam with soln. of **sodium or potassium salts.** G. McP. Smith showed that the action of various salt soln. on the alkali amalgams results in the partial displacement of the alkali in the amalgam by the alkali in the salt soln., and the same equilibrium is obtained by the action of eq. soln. of **potassium, sodium, rubidium, or cæsium chloride** on potassium, sodium, or lithium amalgam. For the reaction $NaHg_n+(m-n)Hg+M^{\cdot}=MHg_n+Na^{\cdot}$, the equilibrium constant is 0·31 when M represents K; 0·37, when M=Rb; and 0·48, when M=Cs. The stability of the alkali amalgams increases in the order of their chemical activity in air, water, or in aq. soln. of the chlorides $LiHg_n$, KHg_n, $RbHg_n$, $CsHg_n$, and $NaHg_n$. S. A. Braley and co-workers, and G. McP. Smith and co-workers also studied the action of mixed alkali salt soln. H. Davy found that moist **ammonium salts** with potassium amalgam give a potassium salt and ammonium amalgam. According to J. Proude and W. H. Wood, sodium amalgam does not give ammonium amalgam with aq. **ammonia,** with ammoniacal soln. of **sodium hydrophosphate; calcium**

chloride ; **magnesium sulphate** ; molten **ammonium sulphate, nitrate,** or **acetate ;** or with **ethyl or methyl alcoholic soln. of ammonium chloride, oxalate, acetate, benzoate, tartrate, or succinate ;** but it does so with soln. of **phenol** or **pyrogallol** in ammonia.

M. Rosenfeld found that when a stream of air is passed over molten potassium amalgam, a grey ash remains ; this becomes brownish-red when heated to a higher temp. H. Davy found that the solid amalgam loses its mercury at a red heat, and V. Merz and W. Weith, that potassium amalgam is more rapidly decomposed by heat than is sodium amalgam. When the alkali amalgam is distilled, H. Davy found it to be very difficult to obtain a complete separation.

D. Tommasi found that **potassium chlorate** is not reduced by sodium amalgam ; E. Fromm and O. Gaupp, that **sulphuryl chloride** is not reduced in petroleum ether soln., but is vigorously reduced in ethereal soln. ; T. Curtius and A. Darapsky, that **azoimide** is not reduced in alkaline soln. ; A. R. Hantzsch and L. Kaufmann, that **sodium nitrite** is reduced to hyponitrite ; E. Frémy, that **arsenious oxide** or an arsenite is reduced to an unstable product which reduces cold potassium permanganate, and salts of copper, silver, gold, or mercury ; and E. A. G. Street, that **chromic acid** is energetically reduced. G. Fernekes found that aq. soln. of **hydrocarbons** react more vigorously with sodium or potassium amalgam than with water, in spite of their low solubility in water ; **amide** soln. act as rapidly as aq. soln. ; **toluidine** and **xylidine** more slowly than in water. Soln. in **alcohols, ketones,** and different kinds of **sugar** were also investigated. E. Fischer, W. Wislicenus, A. von Baeyer, A. H. Salway, etc., have studied the reducing action of sodium amalgam on **organic compounds.** B. Fetkenheuer found **carbon tetrachloride** is quantitatively decomposed by warm sodium amalgam : $4Na+CCl_4=4NaCl+C$. E. Vanstone found that sodium amalgam with a high sodium content is more satisfactory than sodium alone as a reducing agent in organic chemistry, and he recommended an amalgam liquid at 21·4° which contains 85° at. per cent. of sodium.

According to H. Davy, potassium and sodium amalgams readily amalgamate **iron** and **platinum.** Sodium amalgam was found by A. C. Christomanos to convert **zinc, copper,** and platinum into their amalgams, but not so readily **magnesium.** E. Ramann found **ferric oxide** is readily attacked by sodium amalgam. W. Crookes,[9] H. Wurtz, J. Nicklès, E. P. H. Vaughan, J. B. Thomson, E. Silliman, and L. P. Cailletet have discussed the use of sodium amalgam in the extraction of gold.

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§ 40. Amalgams of Copper, Silver, and Gold

W. J. Humphreys [1] found that copper dissolves very sparingly in mercury, at room temp. H. Iggena found the percentage solubility to be 0·16 ; T. W. Richards and R. N. G. Thomas, 0·0024 per cent. ; and A. Gouy, 0·001 per cent. E. N. Horsford said that copper is not permeable to mercury, but J. Nicklès, and A. Knop found it to be slightly permeable and the metal to become brittle, but C. Diezel found that some varieties of copper do not become friable. A piece of copper foil in a soln. of mercuric nitrate is gradually penetrated by the precipitated mercury, and thus becomes brittle ; R. Lacau used an acidified soln. of mercuric nitrate ; W. J. Humphreys found that copper diffuses rapidly in mercury. N. A. Puschin said that the chemical nature of copper is not altered when diluted with mercury. J. P. Joule said that the amalgam prepared by electrolysis, and by dissolving copper in mercury, has the composition of **copper mercuride,** CuHg ; but the evidence for the individuality of this product is meagre. J. Schumann said the sp. gr. is 12·655, while that calculated on the assumption that the product is a mixture, is 12·00.

The preparation of copper amalgam.—R. Boyle, and W. Lewis obtained copper amalgam by triturating mercury with verdigris and common salt ; the former used a little vinegar, and purified the product by washing. J. Schumann

failed to verify these observations. J. P. Joule prepared an amalgam approximating to CuHg, by dissolving copper in mercury, and removing the excess of the latter by strong press. W. Ramsay, and D. Reichinstein and A. Bürger stated that copper readily amalgamates with mercury, if the surface of the copper be cleaned with dil. sulphuric acid, washed with distilled water, and dried with filter paper; a little of dry mercury is then rubbed over the surface of the copper and the excess of mercury removed. E. and A. C. Becquerel allowed a strip of copper to stand in contact with mercurous chloride immersed in distilled water. J. J. Berzelius, R. B. Boulton, M. Gersheim, C. R. König, M. Pettenkofer, etc., triturated copper dust reduced from the oxide by carbon monoxide or precipitated from a soln. of the sulphate by zinc or iron, with mercury and a few drops of mercurous nitrate, or with a mush of mercuric sulphate and water at 60°–70°. E. W. Jungner used a modification of this process. J. Schumann precipitated the copper from the cupric sulphate soln. while in contact with mercury. A. C. Christomanos brought the copper sheet in contact with ammonium amalgam; C. Klauer, and J. Schumann used one per cent. sodium amalgam in a soln. of cupric sulphate; R. Böttger used a conc. soln. of cupric sulphate and ammonium chloride; and A. A. Damour, zinc amalgam in an ammoniacal soln. of cupric sulphate. W. R. Grove, J. P. Joule, H. Iggena, J. Schumann, and A. Guntz and M. de Grieft, prepared copper amalgam by the electrolysis of a soln. of cupric sulphate with a mercury cathode. C. Paal and H. Steyer prepared **colloidal copper amalgam** by shaking copper hydrosol with mercury, or by mixing copper and mercury hydrosols.

The properties of copper amalgam.—The **colour** of copper amalgam varies from silver-white to a golden-yellow, and to a light red. J. P. Joule, H. Iggena, and J. Schumann obtained **crystals,** which A. C. Becquerel regarded as rhombic prisms with pyramidal ends. P. I. Bachmetjeff found that a contraction in volume attends the formation of copper amalgam. J. Schumann found that a 13·4 per cent. amalgam has a **specific gravity** of 12·653 when liquid, and, after solidification, 12·90; while an amalgam approximating to HgCu has a sp. gr. 12·655—the values calculated from the mixture rule are respectively 12·37 and 12·00. J. P. Joule found for the sp. gr. of copper amalgams:

Hg (per cent.) . .	81·63	80·20	80·00	78·36	76·13	77·52	74·52	71·63
Sp. gr. . . .	13·32	13·26	13·185	13·17	13·51	13·76	13·01	12·99

G. Meyer measured the **surface tension** of a 0·00505 per cent. copper amalgam against salt soln. E. von Schweidler measured the coeff. of **viscosity** of a 0·5 per cent. copper amalgam and found the value 0·01620 with a temp. coeff. $\eta=1-0·00302\theta+0·0000025\theta^2$. According to A. Guntz and M. de Grieft, amalgams containing 14 per cent. of copper, Hg_3Cu_2, up to 24·10 per cent. of copper, HgCu, may be prepared by a **pressure** of 6250 kgrms. per sq. cm., and by the same press. with boiling mercury, amalgams with 45 to 97 per cent. of copper have been made. J. Schumann found the **cubical expansion** between 17° and 155° is 3·1 per cent. for a 13·4 per cent. amalgam, and 6·6 per cent. for the amalgam approximating to CuHg. According to A. Guntz and M. de Grieft, the **melting point** of the amalgam approximating HgCu is approximately 135°. E. de Souza said that the **action of heat** on copper amalgam furnishes $HgCu_{16}$ in a bath of sulphur vapour, $HgCu_{14}$, in the vapour of mercury and in the vapour of diphenylamine; but V. Merz and W. Weith found that after 8 hrs. in a sulphur vapour-bath, or 24 hrs. in a mercury vapour-bath, the product is virtually pure copper, and only 0·66 per cent. of mercury remained in an amalgam heated 22 hrs. in a diphenylamine-bath. T. W. Richards and S. K. Singer found that all the mercury can be volatilized over 350° in a stream of hydrogen, and that a trace of copper is volatilized at a higher temp. A. Coehn and A. Lotz found copper amalgam in vacuo is positively charged when in contact with glass. A. Battelli, and A. P. Schleicher measured the **electrical resistance;** G. Meyer obtained evidence of the ionization of both copper and mercury in the dil. amalgam. G. Meyer measured the **electromotive force** in

soln. of *sodium hydroxide, potassium cyanide, sulphuric acid, hydrochloric acid, potassium iodide, sodium carbonate, magnesium sulphate,* and *lead acetate ;* V. Rothmund, with N-H_2SO_4, and $\frac{1}{200}N$-$CuSO_4$; N. A. Puschin, Cu | N-$CuSO_4.5H_2O$ | $CuHg_n$; C. Hockin and H. A. Taylor, $CuHg_n$ | dil.H_2SO_4 | $ZnHg_n$; and J. F. Spencer, with N-soln. of *cupric salts.* E. Cohen, F. D. Chattaway, and W. Tombrock found the e.m.f. of cells with copper amalgam is independent of the conc. between 1 and 16 per cent. of copper ; C. R. A. Wright, D. Reichinstein and A. Bürger, and G. Gore have also studied this question. J. Roszkowsky measured the hydrogen polarization with copper amalgam as cathode. L. W. Oholm investigated the e.m.f. of cells with copper amalgam in cupric sulphate soln. against mercury and mercuric sulphate. R. Lacau found that the surface of amalgamated copper retains its lustre in acidic soln., but in air or water, it soon turns greenish-grey ; and A. Vogel found that the surface of copper amalgamated not too thickly loses its metallic film after 12 hrs.' exposure to air. M. Pettenkofer found that hot water, dil. acids or alkalies, alcohol, or ether do not attack copper amalgam. According to M. Pettenkofer, and W. F. A. Thomæ, copper amalgams have been used in making blocks for printing diagrams, and as dental cement, and in the amalgamation process for gold. J. Alemany has discussed the use of amalgamated copper cathode in place of the mercury cathode for analytical work.

Silver amalgams.—The power possessed by mercury of " licking up " gold and silver must have been known from early times. Pliny, in his *Historia naturalis,* refers to the amalgamation of gold. According to A. Cronstedt,[2] *silver amalgam*—or simply, *amalgam,* or *argental*—was found as a mineral at Sala (Sweden) about 1660. The native amalgam has since then been reported from many other localities, and in some cases given special names—*arquerite,* from Arqueros in Chile ; *bordosite,* from Bordos in Chile ; and *kongsbergite,* from Kongsberg in Norway. The reported analyses range from Ag : Hg=18·64 : 81·36 to 95·8 : 3·6 per cent.

According to J. F. Daniell,[3] when a silver rod is immersed in mercury at ordinary temp., a little is dissolved in the course of 24 hrs., but the rod remains malleable—even in 6 weeks, very little silver is dissolved by the mercury ; but if the mercury be gradually heated to its b.p., and then slowly cooled, soft acicular crystals of an amalgam are deposited on the silver rod near the surface of the mercury. W. Haidinger reported that the two metals unite very slowly and that the silver becomes crystalline and brittle, and not infrequently covered with large crystals. Such crystals of amalgam were found by J. B. A. Dumas, G. Küstel, and C. A. Kenngott, in the mercury wells where amalgamation processes are used. A. Ogg found a little silver dissolved in mercury at room temp. W. J. Humphreys said that 0·05 per cent. is dissolved at 27°, and more at a higher temp., as observed by J. B. L. Romé de l'Isle. A. Gouy also measured the solubility of silver in mercury, and found it rises rapidly with temp. W. Reinders dissolved about 2 per cent. of silver in mercury ; and A. Feodoroff, about 6 per cent. in an open vessel. E. Maey showed that the amalgams cannot be prepared in any desired proportion by melting the constituents together, because the m.p. of silver is so much higher than that of mercury, and the solid amalgam is but sparingly soluble in mercury ; he obtained an amalgam by dissolving silver in heated mercury, poured off the liquid amalgam, and after cooling, removed the liquid from the solid amalgam by press. W. J. Humphreys found the rate of diffusion of silver in mercury to be very rapid—20 mm. per minute.

K. A. Winkler found that mercury has scarcely any action on silver oxide or silver silicate at ordinary temp., and that silver amalgam and mercuric sulphide are formed when mercury and silver sulphide are triturated together for a long time ; silver chloride also when triturated with mercury and water behaves similarly, and the presence of a little sodium chloride or sulphate accelerates the reaction, and the reaction is quite rapid if some powdered iron be present ; copper acts in the same way but less vigorously ; silver sulphate and mercury similarly form mercurous sulphate and silver amalgam. J. W. Mallet and R. Segura found that precipitated silver

sulphide or native argentite is reduced to silver amalgam and mercuric sulphide when triturated with mercury and water; the amalgamation proceeds faster with a small than with a large proportion of water. J. H. Croockewit, J. Schumann, J. P. Joule, L. Arons, and S. Lindeck found that a not too conc. soln. of silver nitrate is reduced by mercury, and that the precipitated silver unites with a portion of the mercury, forming a crystalline amalgam in the form which J. B. L. Romé de l'Isle said is *très-connu sous le nom d'arbre de Diane—silver-tree*, or *arbor dianæ*. If the proportion of mercury be too large, the product is liquid, not crystalline, and to form the tree mercury amalgamated with one-eighth of silver was recommended by M. H. Klaproth, G. Küstel, and J. J. Berzelius, but J. L. Proust found mercury alone acts as well. A little free acid accelerates the reaction. A. Ogg studied the equilibrium conditions between mercury and soln. of silver nitrate, and obtained results in accord with $2Hg+2Ag^{\cdot}\rightleftharpoons 2Ag+Hg^{\cdot}-Hg^{\cdot}$, and not $Hg+Ag^{\cdot}\rightleftharpoons Hg^{\cdot}+Ag$. J. B. Vitalis, and F. Fouqué and A. M. Lévy used a soln. containing both silver and mercury nitrates. D. Dehne analyzed a silver-tree with 81·36 per cent. of silver. F. L. Hünefeld found that if mercury be left for a long time at the bottom of a dil. soln. of silver nitrate, the silver-tree first formed is dissolved by the underlying liquid amalgam, and after a time, long four-sided lustrous prisms containing 68·3 per cent. of silver were formed. R. Böttger also prepared silver amalgam by the action of sodium amalgam on a soln. of a silver salt.

G. Campani found that silver, particularly if finely divided, precipitates mercury and forms an amalgam when added to a soln. of mercuric chloride, or of potassium mercuric iodide, at ordinary temp. H. C. Jones claimed to have made silver amalgams of definite composition by preparing a double salt of a definite mixture of salts of the two metals with the subsequent reduction in the cold. When mercuric chloride, for example, acts on either silver or mercury, or an amalgam of the two metals, each atom of either metal combines with a mol. of mercuric chloride. The chloride is then reduced by means of a soln. of ferrous oxalate mixed with an excess of potassium oxalate to keep the iron salts in soln. A soln. of sodium sulphite may also be used as the reducing agent. A. C. Becquerel obtained crystals of silver amalgam by allowing soln. of silver and mercurous nitrates to be separated by a cracked glass tube. W. Reinders obtained silver amalgam by shaking a mixed soln. of mercurous and silver nitrates with mercury. A. C. Becquerel also allowed a mixture of mercurous and silver chlorides to stand under water with a strip of amalgamated copper for some days. J. P. Joule, J. Schumann, and C. Luckow made silver amalgam by the electrolysis soln. of silver salts with a mercury cathode.

Over a dozen chemical compounds have been reported with formulæ based upon analyses, but for most of them there is very little evidence which would justify their being recognized as chemical individuals. For example, the native mineral *arquerite* has been given the formula $HgAg_{12}$, based upon the analyses of P. Berthier, and I. Domeyko; and the formula Hg_3Ag_2 based on the analyses of J. G. Schreiber, V. Cordier, J. C. H. Heyer, A. Lacroix, etc., has been assigned to native amalgam. Analyses of a native amalgam from Sala by H. Sjögren corresponded with Hg_6Ag_5—the sp. gr. was 11·56, *vide supra*, the occurrence of silver amalgam. J. H. Croockewit obtained products with compositions corresponding with Hg_4Ag_2, Hg_8Ag_5, Hg_3Ag_2, and HgAg; H. C. Jones, with $Hg_{31}Ag$, $Hg_{15}Ag$, $Hg_{11}Ag$, Hg_7Ag, Hg_5Ag, Hg_3Ag, Hg_2Ag, and HgAg; and F. T. Littleton, with Hg_4Ag, which he said has a heat of formation of 3432 cals., and a sp. ht. of 0·029 when the value calculated from the mixture law is 0·0359. The latter also said that the heat of formation of Hg_2Ag from silver foil is 1·53 Cals., and from silver crystals —0·40 Cal. F. L. Hünefeld claimed to have made a compound Ag_4Hg by the action of mercury on a soln. of silver nitrate until the silver-tree first formed has dissolved, and the liquid amalgam has crystallized.

According to E. Maey, the change in the sp. vol. with the conc. of silver amalgam gives a curve which has a break near the value calculated for HgAg, while A. Ogg believes that the composition is better represented by Hg_4Ag_3. The curve showing the relation between the composition of the amalgam and the vapour pressure shows

the existence of **silver tetratritamercuride,** Hg_4Ag_3, and HgAg ; and, according to A. Ogg, K. Bornemann, and R. A. Joyner, in an evacuated vessel, the equilibrium between silver and silver saturated with mercury corresponds with Hg_4Ag_3. W. Reinders obtained large needle-like crystals of Hg_4Ag_3 by shaking mixed soln. of silver and mercurous nitrates in which $AgNO_3$=0·57 to 0·61 ($AgNO_3$+$HgNO_3$) at 25° for 12 to 20 days. According to A. Ogg, the heat of formation is 7336 cals. per mol.

M. H. Klaproth's analyses of a native amalgam from Moschellandsberg corresponded with HgAg. A. Feodoroff's cooling curves of silver amalgams showed that those with a composition, **silver mercuride,** AgHg, are probably eutectic mixtures. W. Reinders believed that in all probability HgAg does not represent a true compound, while K. Bornemann thought it did. W. Ramsay said that amalgams have this composition after heating to dark redness. J. H. Croockewit claimed to have made an amalgam of this composition by reducing a moderately conc. soln. of silver nitrate with mercury, and H. C. Jones, by the action of silver, or silver-amalgam on a soln. of mercuric chloride. The latter said the sp. gr. is 12·8099 at 20°/20.

According to W. Reinders, the products Hg_4Ag_3 and **silver ditritamercuride,** Hg_2Ag_3, separate from a mixture of mercury, and soln. of mercurous nitrate and an excess of silver nitrate, in the proportions $AgNO_3$=0·87 to 1·00 ($AgNO_3$+$HgNO_3$) for 5·30 days at 25° ; or by shaking finely divided silver for 7–19 days with an excess of a soln. of mercurous nitrate. The crystals of the latter have a reddish tinge ; those of the former a bluish tinge. The product also appears as a pale grey powder. R. Müller and R. Hönig made metallic needles of **silver trihemimercuride,** Ag_2Hg_3, by keeping a drop of mercury in contact with a soln. of silver nitrate and cuprous iodide in dry pyridine. W. Reinders also claimed to have obtained evidence of the formation of a compound **silver tritamercuride,** Ag_3Hg.

According to E. Maey, silver amalgams with 0·13 per cent. of silver are liquid at 17·5° ; one with 10 per cent. of silver was a mush of liquid crystals ; and amalgams with more than this amount of silver are solid. According to J. P. Joule, the sp. gr. of some amalgams are :

Silver . .	34·5	51·6	53·5	60·9	74·6	72·3 per cent.
Sp. gr. . .	14·68	12·49	13·25	12·34	12·54	11·42

According to E. Maey, the sp. gr. of amalgams with up to 29·5 per cent. of silver is almost the same as that of mercury, and the sp. vol. is nearly 0·07380 ; and with amalgams containing from 9·751 to 37·0 per cent. of silver, the sp. gr. falls from 13·197 to 9·751, and the sp. vol. v is given by v=0·0577+0·000477w, where w denotes the per cent. of silver. Amalgams with 77·5 per cent. of silver were obtained by compression, and more mercury can be removed by compressing the warm amalgam —at 100°, an amalgam with 70 per cent. of mercury was formed, and at higher temp., one with 61 per cent. of mercury was produced. Amalgams with still less mercury were obtained by evaporating off the mercury. A. Ogg found that the vap. press. of amalgams containing an excess of mercury is very nearly equal to that of pure mercury, but falls very considerably when the composition approaches Hg_4Ag_3, and the amalgam is in equilibrium with mercury. W. Ramsay found the vap. press. of an amalgam was lowered 22·8 mm. by the dissolution of 3·22 grm.-atoms of silver in 100 of mercury, and if the silver were atomic, this would correspond with an at. wt. 112·4. E. D. Eastman and J. H. Hildebrand found silver to be very sparingly soluble in mercury at 318°, and an amalgam with 1·27 per cent. of silver has a normal vap. press. in accord with Raoult's law. E. Beckmann and O. Liesche applied the b.p. method of determining the mol. wt. of silver in mercury and the results agree with the view that silver is monatomic. A. Matthiessen and C. Vogt, and N. Parravano and P. Jovanovich, have measured the electrical resistance of silver amalgams ; while C. L. Weber found the sp. resistance R, referred to mercury at 18°, to be :

	0·25 per cent. Ag			0·5 per cent. Ag.			1·0 per cent. Ag.		
R . .	17·2°	37·8°	39·8°	17·2°	18°	42·9°	16·1°	18·0°	43·3°
R . .	0·9948	1·0188	1·0276	1·0009	0·9984	1·0245	0·9811	0·9930	1·0105

A. Battelli found the differences between the observed and calculated sp. resistances are negative and increase with increasing proportions of silver, and are positive with Hg : Ag=400 : 1 ; with higher proportions of silver the resistance becomes negative. A. R. Calvo found that for very dil. amalgams with up to 0·06 per cent. of silver, between 0° and 20°, the electrical resistance is a linear function of the conc., and at higher temp. the resistance then furnishes a curve concave to the conc. axis. W. Reinders found that liquid amalgams containing 0–0·076 per cent. Ag coexist with soln. in which the silver nitrate is 0–2·5 per cent. of the total salts ; the compound Ag_3Hg_4 coexists with soln. containing from 2·5 to 18 per cent. of silver nitrate ; the compound Ag_3Hg_2 coexists with soln. containing from 18 to 40 per cent. of silver nitrate ; the compound Ag_3Hg coexists with soln. containing from 40 to 100 (nearly) per cent. of silver nitrate ; solid soln. of mercury in silver coexist with soln. containing practically nothing but silver nitrate. The potential difference metal/soln. changes with composition in a manner which is in harmony with the equilibria just described. A. Ogg found the polarization e.m.f. is very nearly equal for soln. of silver and mercurous nitrates, but is lower for mixtures than for either soln. alone ; and silver amalgam is a "nobler" metal than either of its constituents with respect to soln. of mercurous and silver nitrates. S. Lindeck, and G. Gore measured the e.m.f. of silver amalgams, and C. Hockin and H. A. Taylor of amalgamated silver against amalgamated zinc in dil. sulphuric acid. R. Müller and R. Hönig found the e.m.f. of the cell Ag | 0·1 *N*-$AgNO_3$ in pyridine | Hg is 0·038 volt ; but if the pyridine is sat. with cuprous iodide, the e.m.f. is 0·37 volt. L. Arons found that the voltage for the arc lamp is higher with silver amalgam than with mercury alone—the spectrum of silver appears only in the light at the cathode. A. Coehn and A. Lotz found that silver amalgam is positively charged with respect to glass in vacuo.

When silver amalgam is heated, the mercury volatilizes, but, according to J. L. Gay Lussac, some mercury is retained even at the m.p. of silver. E. de Souza found that in a sulphur vapour-bath, the residue contained $HgAg_{13}$; in a mercury vapour-bath, $HgAg_{11}$; and in a diphenylamine-bath, $HgAg_4$; and V. Merz and W. Weith found that if the amalgam be heated in a sulphur vapour-bath for 21, 72, and 100 hrs. there remains respectively 2·3, 1·26, and 1·24 per cent. of silver, and in a diphenylamine-bath for 50 and 78 hrs. there remains respectively 5·4 and 4·4 per cent. of silver. At 200° in a stream of air, G. A. Hulett obtained a distillate with one part of silver in 533,000 parts of mercury ; after a second distillation, 0·03 part of silver in 1,000,000 parts of mercury ; and after a third distillation, no silver could be detected in the distillate. With very carefully regulated heating, D. J. A. Schlosser obtained the residual silver in a dendritic form. C. Brame made a similar observation with respect to silver amalgam as that which he made with respect to silver. C. Hockin and H. A. Taylor made a **silver-copper amalgam,** and measured its e.m.f. against amalgamated zinc or dil. sulphuric acid. The so-called *dental amalgam*, studied by A. W. Gray, is an alloy of silver and tin with may be 5 per cent. copper. For use it is mixed with mercury.

Gold amalgams.—The remarks concerning the early history of silver amalgam are also applicable to gold amalgam. In 1783, J. B. L. Romé de l'Isle [4] reported quadratic prisms of native *gold amalgam*. R. F. Marchand described a sample from Columbia, and, according to F. Schmitz, samples have been reported from almost all districts where gold occurs. Analyses range from 38·39 to 41·63 per cent. of gold ; 57·40 to 60·98 per cent. of mercury ; and with up to 5 per cent. of silver. The formula Au_2Hg_3 has been applied to many native gold amalgams.

According to W. Guertler,[5] the solubility of gold in solid mercury is small. A. Gouy measured the solubility of gold in mercury, and found the solubilities of copper, silver, and gold to be 0·00001, 0·0003, and 0·0013 part of metal per unit weight of amalgam. M. von Wogau found the diffusion coeff. of gold in mercury to be k=8·33 cals. per sq. cm. per sec. at 11° ; while W. C. Roberts-Austen found the diffusion coeff. of mercury in gold to be k=0·72 at 11°. Gold amalgam is slowly

formed by mixing its constituents at ordinary temp., but more rapidly if the temp. is raised—say, by putting red-hot gold plates into mercury. J. F. Daniell stated that a bar of gold dipped in cold mercury quickly turns white, and is soon completely penetrated by mercury, but even after a month the gold remains malleable and is covered by small crystals. With boiling mercury, the gold dissolves, forming a mass with a pasty consistency. M. Faraday, and C. Barfoed noted the volatilization of mercury from the amalgam. W. Skey noted that some grains of native gold resist amalgamation because they are covered with a film of sulphide. The production of amalgam in the extraction of gold has been previously discussed. L. Knaffl recommended precipitated gold for the preparation of amalgams; T. Wilm used dil. sodium amalgam in place of mercury, and washed the product with conc. nitric acid. J. H. Croockewit prepared crystals of what he regarded as Hg_2Au by amalgamation and filtration by pressure through leather. T. H. Henry prepared four-sided prisms of what he regarded as $HgAu_8$ by dissolving one part of gold in 1000 parts of mercury and filtering the soln. through leather. E. de Souza obtained $HgAu_{8 \text{ or } 9}$ as a residue after heating the amalgam in the diphenylamine vapour-bath; and $HgAu_9$, by heating the amalgam in a bath of sulphur or mercury vapour. C. Paal and H. Steyer prepared **colloidal gold amalgam**.

The amalgam with 6 parts of mercury and one of gold crystallizes in four-sided prisms. A. H. Chester obtained hexagonal prismatic crystals by the action of mercury on gold and by dissolving out the excess of mercury with dil. nitric acid. T. Wilm's process furnishes acicular or columnar crystals. W. Ramsay measured the lowering of the vap. press. of mercury by gold, and G. Tammann, the lowering of the f.p. The results in both cases agree with monatomic mols. E. D. Eastman and J. H. Hildebrand measured the vap. press. of gold amalgams at conc. up to 23·7 per cent. of gold. The separation of a solid occurs at a conc. of 16·5 per cent. of gold. With more dil. soln. the vap. press. are greater than accord with Raoult's law. E. Beckmann and O. Liesche found that the b.p. of gold amalgam agrees with the presence of monatomic uncombined gold. N. Parravano made a thermal diagram of amalgams with 0 to 35 per cent. of gold, and obtained a horizontal line at 100°, which was taken to correspond with a reaction between a solid, separating at a higher temp., and the liquid to form a new solid stable at a lower temp. S. A. Braley and R. F. Schneider obtained the results shown graphically in Fig. 46. There are thus two eutectics, and three compounds, **gold hemimercuride,** Au_2Hg, **gold pentahemimercuride,** Au_2Hg_5, and **gold tetramercuride,** $AuHg_4$. A. Matthiessen and C. Vogt, and N. Parravano and P. Jovanovich measured the electrical conductivity of gold amalgams. and found the conductivity at the gold end of a series with less than 10 per cent. of mercury decreases as the proportion of mercury increases. A. Coehn and A. Lotz found gold amalgam in vacuo is positively charged with respect to glass.

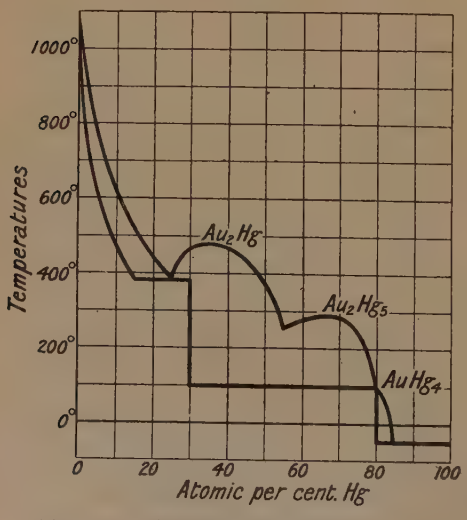

FIG. 46.—Freezing-point Curves of Gold Amalgams.

If gold amalgam be strongly heated, the mercury distils off, and if the rise of temp. be carefully regulated, the gold remains in an arborescent form; L. Knaffl obtained crystals of gold by heating the amalgam to 80°. According to E. de Souza,

if heated to the b.p. of sulphur, or mercury, until the weight is constant, the composition approximates to $HgAu_9$, and to $HgAu_8$ in a bath of diphenylamine. V. Merz and W. Weith found the weight alters with time so that the amalgam contains 1·07 per cent. of mercury after heating 20 hrs. in a bath of sulphur vapour, 0·40 per cent. after 44 hrs.; and 0·33 per cent. after 60 hrs. Similarly, after 24 hrs. in a mercury vapour-bath there remain 2·63 per cent. of mercury; 1·75 per cent. after 75 hrs.; 1·48 per cent. after 114 hrs.; and 1·43 per cent. after 134 hrs. Likewise also in a bath of diphenylamine vapour there remains 7·86 per cent. of mercury after 24 hrs.' heating; 5·3 per cent. after 48 hrs.; and 4·5 per cent. after 75 hrs. G. A. Hulett distilled a sat. gold amalgam and found the distillate had 0·027 part of gold per 1,000,000 parts of mercury; and after repeated distillation only 0·01 part per million.

G. Kasanzeff found the composition of gold amalgam remaining after the action of nitric acid on the liquid amalgam depends on the temp. and conc. of the acid. The yellow or brown residues contain 8·4–18·4 per cent. of mercury. W. Ramsay said that gold amalgam is not very soluble in mercury. J. H. Croockewit found the sp. gr. of crystals of Hg_2Au to be 15·142; F. L. Sonnenschein gave 15·47 for Hg_3Au_2. A. Wehrle prepared a mixed *gold-silver amalgam*, and R. F. Schneider regarded pieces of a mixed amalgam which he obtained from Columbia as containing $Hg_6(Au, Ag)$; W. H. Seamon gave the composition $Au(Hg, Ag)_2$. C. Hockin and H. A. Taylor measured the e.m.f. of a mixed amalgam against amalgamated zinc in dil. sulphuric acid.

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§ 41. The Amalgams of the Metals of the Alkaline Earths

According to L. Maquenne,[1] the affinity of calcium for mercury is small. H. Iggena measured the solubility of barium and strontium in mercury at different temp., and found:

	0°	20°	30°	46°	56°	64·5°	81°	89·5°	
Ba . .	0·144	0·325	0·422	0·519	0·680	0·832	0·967	1·06	per cent.
Sr . .	0·733	1·04	1·27	1·35	1·51	1·79	1·80	1·0	,,

H. Moissan and G. Chavanne found that calcium dissolves but slowly in mercury at ordinary temp., and by shaking the two elements in an atm. free from moisture, a soln. containing 2·5 grms. of calcium per 100 grms. of mercury can be obtained. H. P. Cady, too, heated the two elements up to the b.p. of mercury, and found only a small proportion of calcium was dissolved. M. von Wogau measured the diffusion coeff. k in cals. per sq. cm. per sec., and found for calcium at 10·2° k=6·45 ; for strontium at 9·4°, k=5·44 ; and for barium at 7·8°, k=6·02.

The preparation of amalgams of the alkaline earths.—H. Moissan and G. Chavanne prepared calcium amalgam by shaking 2 grms. of calcium with 100 grms. of mercury in an evacuated sealed tube for 24 hrs. R. Böttger prepared the amalgam of barium and strontium, and C. Klauer that of calcium by immersing one per cent. potassium or sodium in an aq. soln. of the alkaline earth chloride ; the reaction is accompanied by a feeble evolution of gas. The amalgam is removed from the soln. as soon as the evolution of gas has ceased ; dried by press. between bibulous paper ; and preserved under rock oil. G. McP. Smith, W. Crookes, J. Schumann, H. Iggena, employed the process for barium amalgam ; and G. McP. Smith and B. Franz, for strontium amalgam.

H. Davy prepared barium and strontium amalgams by moulding a mixture of the hydroxide, chloride, carbonate, or sulphate with water to form a kind of dish ; placing the vessel on a platinum plate to serve as anode ; filling the vessel with mercury, and using that as cathode. H. Davy, and J. J. Berzelius and M. M. Pontin likewise prepared calcium amalgam by similarly electrolyzing the hydroxide. R. Hare described the preparation of amalgams of the alkaline earths by what he called J. J. Berzelius and M. M. Pontin's process, *i.e.* the electrolysis of aq. soln. of their chlorides, in contact with mercury as cathode. This was one of the early applications of the mercury cathode which was introduced later in analytical work by W. Gibbs. The method was later employed by G. McP. Smith and H. C. Bennett, and P. M. Giesy and J. R. Withrow, who improved many details. R. Bunsen electrolyzed a mixture of barium chloride with a little dil. hydrochloric acid with a mercury cathode. L. Maquenne, H. Iggena, W. Kerp and co-workers, G. Langbein, and G. McP. Smith and co-workers similarly electrolyzed a soln. of the nitrate with a mercury cathode. Strontium and barium amalgams were prepared in a similar way by A. Guntz and G. Röderer, G. McP. Smith and co-workers, H. Iggena, P. Fedotieff, L. Maquenne, W. Kerp and co-workers, and G. Langbein. S. B. Frank and J. R. Withrow prepared solid strontium amalgam by electrolysis, but the same process did not succeed with calcium amalgam. W. Ramsay said that strontium or calcium amalgam prepared by electrolysis is very dil., since it is very readily attacked by water even when the electrolytic cell is surrounded by a freezing mixture. R. Bunsen made calcium amalgam by the process he used for barium amalgam. K. Bornemann and G. von Rauschenplat electrolyzed a soln. of calcium chloride with a carbon anode and mercury cathode. W. Kerp and co-workers, G. Langbein, H. Iggena, L. Maquenne, etc., did not succeed so well with the electrolytic preparation of calcium amalgam as with the amalgam of barium and strontium. H. P. Cady obtained a dil. amalgam by the electrolysis of a boiling soln. of calcium chloride ; H. G. Byers also used a soln. of the chloride. J. Férée used a cell with a diaphragm and a mercury cathode. G. McP. Smith and co-workers electrolyzed a sat. soln. of calcium acetate. B. S. Neuhausen employed the electrolytic process. L. Maquenne concentrated the dil. amalgams by distillation in vacuo ; and A. Guntz and co-workers, G. Langbein, W. Kerp and co-workers, and H. Iggena, by distillation under reduced press. in a stream of hydrogen.

A. Guntz and J. Férée reported that crystals of **barium hexadecamercuride,** $BaHg_{16}$, are formed by pressing the electrolytically prepared amalgam through leather, but neither G. Langbein, nor H. Iggena could obtain such a compound,

and W. Kerp considers that the alleged compound is a mixture of $BaHg_{12}$ and mercury. Similar remarks apply to the **strontium tetradecamercuride,** $SrHg_{14}$, likewise to **barium tridecamercuride,** $BaHg_{13}$, reported to be formed as a solid phase at a temp. not exceeding 30° :

	0°	20°	25°	27·6°	28·1°	29·2°
Ba in liquid	0·15	0·32	0·34	0·35	0·36	0·38 per cent.
Ba in solid	4·60	4·73	4·93	4·75	4·77	4·80 „

The calculated value for $BaHg_{13}$ is 5 per cent. Ba. H. Iggena, and W. Kerp and co-workers obtained similar evidence for **barium dodecamercuride,** $BaHg_{12}$, above 30° :

	30°	46°	56°	65°	81°	99°
Ba in liquid	0·43	0·52	0·68	0·83	0·97	1·26 per cent.
Ba in solid	5·29	5·23	5·26	5·26	5·26	5·34 „

The calculated value for $BaHg_{12}$ is 5·39 per cent. Ba. Similar evidence was obtained for **strontium dodecamercuride,** $SrHg_{12}$, between 0° and 30° :

	0°	20°	30°	46°	64·5°	81°
Sr in liquid	0·73	1·02	1·25	1·33	1·76	—
Sr in solid	3·40	3·33	3·42	3·98	5·33	5·37

when the calculated value for $SrHg_{12}$ is 3·51 per cent. Sr. The strontium salt is stated by W. Kerp and co-workers to crystallize from soln. of any conc. at room temp. The silvery plates begin to decompose at 60° under petroleum, and melt at 70°. G. McP. Smith and H. C. Bennett also prepared these crystals as well as those of $Hg_{12}Ba$ by centrifuging off the excess of mercury. H. Iggena, and W. Kerp and co-workers made the barium salt by crystallization between 30° and 100° ; and A. Guntz and J. Férée by squeezing $BaHg_{16}$ at 200 kgrms. per 5 sq. cm. The crystals of the barium salt are cubic. They do not melt when heated in air, but are energetically oxidized ; they are decomposed by water.

W. Kerp obtained a mixture of a liquid and solid amalgam by keeping electrolytically prepared strontium amalgam for some time from which a product thought to be **strontium henamercuride,** $SrHg_{11}$, was obtained. A. Guntz and G. Röderer separated the two by a centrifuge. G. Langbein also prepared this product. H. Iggena, and W. Kerp and co-workers regarded it as a mixture of the dodecamercuride and a decomposition product from which all the free mercury has not been removed. A. Guntz and J. Férée said it is formed when the tetradecamercuride is subjected to a press. of 200 kgrms. per sq. cm. The crystals, according to G. Langbein, furnish cubes and needles, which, according to A. Guntz, are triclinic, and have the m.p. 125°. They are said to change rapidly on exposure to air, forming a mixture of mercury, mercurous oxide, and strontium oxide and carbonate ; they can be preserved in a dry atm. free from carbon dioxide ; they are decomposed by water, but not so easily as the liquid amalgam ; and when heated in vacuo, mercury begins to distil off at about 150° leaving a residue with the composition Hg_5Sr_2. G. Langbein prepared cubic crystals of **barium henamercuride,** $BaHg_{11}$, which melted at 165°, and behaved like the strontium compound.

H. Moissan and G. Chavanne prepared hexagonal prisms of **calcium octomercuride,** $CaHg_8$, which did not melt when heated in vacuo, but the mercury distilled off, forming an amalgam richer in calcium. H. Iggena, and W. Kerp and co-workers prepared what was supposed to be either **strontium octomercuride,** $SrHg_8$, or the heptamercuride, $SrHg_7$, from the amalgam at about 64°–81°. A. Guntz and G. Röderer obtained hexagonal plates of **strontium hexamercuride,** $SrHg_6$, by distilling mercury from the henamercuride. J. Schürger prepared **calcium pentamercuride,** $CaHg_5$, by heating a mixture of calcium with mercury in an atm. of carbon dioxide at 200°–220°. The compound crystallizes in rhombic prisms or needles. It is a reducing agent, is unaltered at the ordinary temp. by dry hydrogen, nitrogen, or nitrous oxide, and oxidizes slowly in dry air but very quickly in moist air. When heated with dry ammonia at the b.p. of mercury, it is converted into a mixture

of calcium hydride and nitride, which decomposes violently in contact with water, with evolution of hydrogen and ammonia. When heated with nitrous oxide, it is converted into calcium oxide without the formation of nitride or nitrosyl calcium. When heated with phosphine, it yields calcium phosphide and a yellow sublimate of mercury phosphide. A. Guntz and G. Röderer, H. Iggena, and W. Kerp and co-workers obtained **strontium pentahemimercuride,** Sr_2Hg_5, as a residue in the distillation of mercury amalgam. J. Férée prepared **calcium tetratritamercuride,** Ca_3Hg_4, in a similar way. The amalgam is porous and greenish-white; it readily decomposes water. When heated in an atm. of hydrogen, it loses mercury but does not form calcium hydride at 400°; the amalgam is rapidly decomposed by nitrogen at 400°; and it blackens when exposed to air at ordinary temp. owing to the fixation of both oxygen and nitrogen. The only mercuride revealed by L. Cambi and G. Speroni's thermal study of calcium amalgam is **calcium tetramercuride,** $CaHg_4$, melting with decomposition at 266°. At higher temp. there is evidence of a primary separation into mercury and **calcium dimercuride,** $CaHg_2$. G. Langbein inferred from the sp. vol. curve the existence of **strontium monomercuride,** SrHg, and **barium monomercuride,** BaHg, in the respective liquid amalgams. G. McP. Smith obtained evidence of the formation of $CaHg_5$ and $BaHg_6$ from the study of the diffusion constants, and of the surface tension of amalgams.

The properties of the amalgams of the alkaline earths.—G. Langbein stated that strontium amalgam adheres to glass better than barium amalgam. Some chemical properties of the amalgams of the alkaline earths have been indicated above. G. Langbein said that the **coefficient of thermal expansion** of strontium amalgam, $\alpha=0{\cdot}000181+0{\cdot}000008w$, when w is the percentage by weight of strontium, is not very different from that of mercury alone; similarly with barium amalgam, where $\alpha=0{\cdot}000181+0{\cdot}000023$. Mixtures containing over 14 at. per cent. of calcium were found by L. Cambi and G. Speroni to have a **melting point** above the b.p. of mercury at ordinary press. W. Ramsay measured the **vapour pressure** of calcium in mercury and obtained a mol. wt. of 19·0 (theory, 40·08); and for barium 75·7 (theory, 137). E. Beckmann and O. Liesche found the effect of calcium on the b.p. of mercury corresponded with the formation of *calcium decamercuride*, $CaHg_{10}$, at these temp. K. Bornemann and G. von Rauschenplat obtained for the **specific resistance,** R, and **specific conductivity,** C, of a 0·12 per cent. calcium amalgam at 0°:

	50°	100°	150°	200°	250°	300°
$R\times10^4$ . .	0·9702	1·0178	1·0680	1·1250	1·1843	1·2600
$C\times10^{-4}$ . .	1·0307	0·9285	0·9363	0·8897	0·8444	0·7937

with a temp. coeff. $0{\cdot}1032\times10^{-6}$ between 50° and 200°; and $0{\cdot}1350\times10^{-6}$ between 200° and 300°. H. P. Cady, A. Schöller, M. le Blanc, and G. McP. Smith measured the **electromotive force** of amalgams of the alkaline earths—the latter found for 0·0439 per cent. calcium amalgam at 23° in 0·1*N*-LiCl, 1·2 volt against 0·088 per cent. strontium amalgam, and 0·107 volt against 0·1385 per cent. barium amalgam; and the same strontium amalgam against the barium amalgam 0·08 volt. L. Cambi measured the e.m.f. of calcium amalgams in methyl alcoholic soln. of calcium chloride at −80°. There is evidence of an abrupt increase in voltage corresponding with $CaHg_4$, and a less marked increase with **calcium enneamercuride,** $CaHg_9$. There is no evidence of the latter on the fusion curve because its temp. of formation is near −41° when the two arrests in the cooling curve are superposed. L. Cambi made similar measurements with pyridine soln. at 25°. S. B. Frank and J. R. Withrow studied the electro-endosmosis of calcium amalgam.

According to J. J. Berzelius and M. M. Pontin, when calcium amalgam is exposed to **air** it is soon covered by a black film of mercurous and calcium oxides; but, according to H. Moissan and G. Chavanne, the film is mercury and calcium oxide. The amalgam is stable in dry air reacting neither with nitrogen nor oxygen. W. Ramsay, J. Férée, and G. McP. Smith have also noted the instability of calcium

amalgam in air; and L. Maquenne found it to be more readily oxidized than strontium amalgam. B. Franz found strontium amalgam to be less stable than barium or sodium amalgam when exposed to air, and W. Ramsay, H. Iggena, G. Langbein, and G. McP. Smith have shown the ready oxidation of this amalgam in air. A. Guntz and G. Röderer said that 6–10 per cent. strontium amalgams are not much affected by exposure to air. J. J. Berzelius and M. M. Pontin, R. Böttger, G. Langbein, H. Iggena, W. Kerp and co-workers, and J. Schumann noted the oxidation of barium amalgam in air. L. Maquenne said that a 25 per cent. barium amalgam oxidizes rapidly in moist air with the development of much heat, but it may be preserved in vacuo or in an inert gas. Calcium amalgam is to be kept in an atm. of **hydrogen** or **carbon dioxide.** *Vide supra* for the action of hydrogen on calcium amalgam. B. Franz said strontium amalgam furnishes strontium when heated in a stream of hydrogen. A. Guntz found that barium amalgam forms barium hydride, BaH_2, of a high degree of purity when heated in an atm. of hydrogen in an iron vessel to 1400°, and strontium amalgam requires a higher temp. to form the hydride. J. J. Berzelius and M. M. Pontin, and H. Moissan and G. Chavanne found that calcium amalgam is slowly decomposed by **water**, forming mercury, calcium hydroxide, and hydrogen; G. McP. Smith found that calcium amalgam is attacked by water more readily than strontium or barium amalgam. H. Iggena, and W. Kerp and co-workers noted the decomposition of water by strontium amalgam—G. Langbein said that with a 27 per cent. strontium amalgam, or a 33 per cent. barium amalgam, the attack is vigorous, and L. Maquenne that a 25 per cent. barium amalgam attacks water rapidly. According to H. Moissan and G. Chavanne, aq. soln. of **mineral acids** attack calcium amalgam like they do sodium amalgam; it reduces an aq. soln. of **alkali nitrate** to ammonia and a trace of nitrite. L. Maquenne found that barium amalgam has scarcely any reducing action on an aq. soln. of **sodium nitrite.** H. Moissan and G. Chavanne found that when calcium amalgam is treated with a soln. of **ammonium sulphate,** ammonium amalgam is formed. R. Böttger also noted the formation of ammonium amalgam when barium amalgam is treated with a soln. of **ammonium chloride.** H. G. Byers also noted the reaction of calcium amalgam as an electrode with soln. of alkali nitrate, **potassium chloride,** or **barium chloride;** and there is an equilibrium condition between calcium amalgam, and **sodium salts** in which the formation of sodium amalgam is involved. G. Fernekes found that very little, if any, barium is replaced by alkali with soln. of sodium or potassium chloride; and G. McP. Smith found a soln. of hydroxide acts more quickly. According to R. Böttger, when a globule of amalgam is placed in a sat. soln. of **cupric sulphate,** it immediately begins to rotate, causing the soln. to move in two opposite directions, and at the same time, barium sulphate shoots out in flakes which assume various hues, from the presence of hydrated cuprous and cupric oxides, and have the appearance of a growth of moss; the action goes on 15–20 mins., by which time the barium is all converted into sulphate. L. Maquenne found that when calcium is heated in a stream of **nitrogen,** a grey amorphous mass is formed which furnishes ammonia when treated with water; according to J. Férée, the product is calcium nitride; L. Maquenne obtained in a similar way strontium nitride and barium nitride—both free from mercury. J. J. Berzelius and M. M. Pontin did not succeed in amalgamating **iron** with calcium amalgam. H. Moissan and G. Chavanne found that calcium amalgam transforms **acetone** into a mixture of isopropyl alcohol and pinacone; and that it does not act on **benzene** dissolved in a moist ether.

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§ 42. The Amalgams of Beryllium and Magnesium

L. F. Nilson and O. Pettersson [1] prepared **beryllium amalgam** by the electrolysis of a conc. soln. of beryllium chloride with a mercury cathode. According to W. Ramsay, the amalgam so prepared is very dil., since more conc. amalgams are readily attacked by the electrolyte ; and it is readily oxidized in air.

H. Davy [2] prepared **magnesium amalgam** by the electrolytic process used for barium amalgam, but, according to W. Kerp and co-workers, the electrolytic process is not satisfactory. A. A. B. Bussy stated that magnesium combines with mercury only when heated, forming a solid amalgam even with a large proportion of mercury. J. A. Wanklyn and E. T. Chapman stated that the two elements unite slowly in the cold, but rapidly and vigorously at the b.p. of mercury. T. Evans and W. C. Fetsch made an amalgam by triturating magnesium powder with 18 times its weight of mercury in a warm mortar. Silvery crystals approximating to Hg_2Mg separate from the amalgam so prepared. The two elements unite at ordinary temp. ; the reaction starts slowly, but the heat which is evolved accelerates the reaction. J. Parkinson, W. Ramsay, J. Schumann, H. Fleck and L. L. Bassett, W. J. Humphreys, H. Iggena, W. Kerp and co-workers, and A. C. Christomanos employed modifications of these processes for the preparation of magnesium amalgam. L. Cambi and G. Speroni made amalgams by dissolving clean magnesium in mercury boiling in a Jena glass vessel in an atm. of nitrogen ; and also by heating mixtures of the two elements in a sealed tube at 390°–400° for 36–48 hrs. Amalgams with more magnesium than the atomic ratio Mg : Hg are difficult to get uniform. C. Klauer made it by the action of potassium amalgam on a soln. of magnesium sulphate, and J. Schumann used sodium amalgam. A. C. Christomanos said that, unlike zinc, copper, and platinum, magnesium is not amalgamated by sodium or ammonium amalgam except sporadically after rubbing the metal with the amalgam for a long time. A. Schmidt and K. Seubert passed the vapour of mercuric chloride over molten magnesium, and also heated a mixture of mercurous chloride and magnesium filings.

H. Iggena, and W. Kerp and co-workers separated crystals of what they regarded as **magnesium hexamercuride,** $MgHg_6$, by rapidly filtering magnesium amalgam. P. I. Bachmetjeff and J. V. Wsharoff thought that **magnesium tetramercuride,** $MgHg_4$, probably exists since the sp. ht. of this amalgam is greater than corresponds with the mixture rule. As indicated above, T. Evans and W. C. Fetsch obtained an amalgam corresponding with **magnesium dimercuride,** $MgHg_2$. L. Cambi measured the e.m.f. of magnesium amalgams and soln. of magnesium chloride and iodide in methyl alcohol at −80°, and in pyridine, and found an abrupt

change in the curve corresponding with $MgHg_2$. R. P. Beck measured the potential differences of magnesium amalgams in 0·1982*N*-soln. of magnesium chloride in ethyl alcohol.

According to H. Fleck and L. L. Bassett, amalgams with 2 per cent. of magnesium are solid and crystalline; and R. S. Willows stated that an amalgam with less than one per cent. of magnesium was solid, and possessed a **melting point** of 170°. L. Cambi and G. Speroni found that the m.p. of an amalgam with 30 per cent. of Mg is higher than the b.p. of mercury. L. Cambi and G. Speroni's thermal study of these amalgams showed the presence of $MgHg_2$, melting with decomposition at 168°; but they did not follow the curve past MgHg. They considered the analogies in the binary systems Ca—Hg and Mg—Hg. A. Smits and R. P. Beck explored the m.p.-composition curves, Fig. 47, and found magnesium dimercuride, $MgHg_2$; **magnesium mercuride,** MgHg; **magnesium ditritamercuride,** Mg_3Hg_2; **magnesium hemimercuride,** Mg_2Hg; **magnesium tritamercuride,** Mg_3Hg; and possibly **magnesium trihemimercuride,** Mg_2Hg_3; but not the hexa- and tetra-mercurides. R. P. Beck also discussed this subject; the existence of R. Kremann and R. Müller's *magnesium decitamercuride*, $HgMg_{10}$, was disproved. P. I. Bachmetjeff and J. V. Wsharoff observed no definite m.p. with the solid amalgams; they also made observations on the **specific heat.** R. P. Beck measured the **vapour pressure** of magnesium amalgams; and W. Ramsay determined the lowering of the vap. press. of mercury by magnesium and obtained a mol. wt. between 21·5 and 24·0 in agreement with the theoretical 24·3 for a monatomic molecule. E. Beckmann and O. Liesche studied the effect of magnesium on the b.p. of mercury. R. S. Willows found the curve for the change of **electrical resistance** with temp. of one per cent. amalgam, is practically a straight line up to 110°, and above that temp. the increase of the resistance is slightly faster than the rise of temp. Unlike the results with zinc and cadmium amalgams, the resistance is the same whether the metal is being heated or cooled. M. le Blanc, R. Kremann and R. Müller, G. Babarovsky, L. Cambi, R. P. Beck, and G. Gore measured the **electromotive force** of magnesium amalgams.

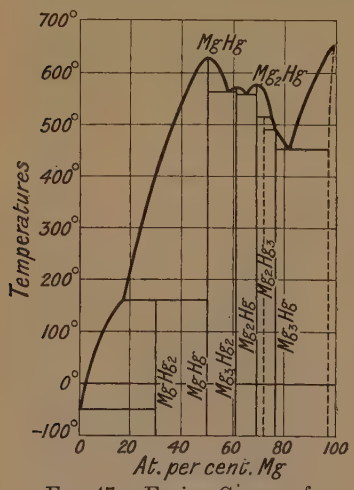

FIG. 47.—Fusion Curves of Magnesium Amalgams.

According to J. A. Wanklyn and E. T. Chapman, an amalgam with 0·5 per cent. of magnesium swells up and becomes matt when exposed to **air,** but, added W. J. Humphreys, the amalgam is not attacked by dry air. G. le Bon found that $\frac{1}{14000}$th part of magnesium in mercury is oxidized in air; and G. Gore found that an amalgam with $\frac{1}{1605}$th of magnesium is quickly covered by a black layer of what he regarded as magnesium suboxide, but this is more probably a mixture of mercury and magnesia. J. Parkinson, W. Ramsay, H. Iggena, and W. Kerp and co-workers also noted how quickly magnesium is oxidized when amalgamated with mercury. H. Davy stated that magnesium amalgam is slowly oxidized by **water,** and rapidly by acidulated water. When mercury is amalgamated with magnesium it acquires the property of decomposing water at ordinary temp.; according to G. le Bon, $\frac{1}{14000}$th of magnesium has an appreciable influence, and magnesium contaminated with mercury also decomposes cold water rapidly. J. Schumann, A. C. Christomanos, H. Iggena, J. Parkinson, T. Evans and W. C. Fetsch, and W. Kerp and co-workers have made observations on this subject. J. A. Wanklyn and E. T. Chapman said that 0·5 per cent. magnesium amalgam decomposes water faster than one per cent. sodium amalgam. T. Evans and W. C. Fetsch observed that

magnesium amalgam has scarcely any action on **alcohol**; but L. Meunier said that magnesium ethoxide is formed and hydrogen evolved with absolute alcohol. M. P. Voronkoff, V. E. Tischtschenko and A. A. Grigorjeff, and A. Kling and P. Roy studied the reducing action of magnesium amalgam on **aldehyde**; F. Couturier and L. Meunier on **acetone**; L. Bouveault and R. Locquin, on **dimethylketone**; H. Fleck, on **alkyl iodides**; T. Evans and co-workers, and M. Chavassieu, on aromatic **nitro-derivatives.** A. G. Loomis studied the ternary system Mg—Hg—NH_3.

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§ 43. The Amalgams of Zinc and Cadmium

The solubility of cadmium is much greater than that of zinc in mercury H. Iggena [1] found the solubilities of zinc and cadmium in mercury to be :

	0°	25°	35°	56°	64·5°	73°	99°	
Zn . .	1·63	2·15	—	3·20	3·49	—	4·73	per cent.
Cd . .	3·27	5·92	7·52	11·53	—	15·89	24·42	„

The presence of copper did not influence the solubility of zinc in mercury. A. Gouy also measured the solubilities between 15° and 18°, and found 0·018 and 0·040 for the ratio of the amount of zinc or cadmium dissolved to the total weight. W. Kerp and co-workers found these numbers too small. J. L. Crenshaw gave 2·2199 grms. per 100 grms. of mercury for the solubility of zinc at 25°; and G. A. Hulett and R. E. de Lury, 5·574 grms. per 100 grms. of mercury for the solubility of cadmium at 25°. W. J. Humphreys measured the velocity of diffusion of zinc in mercury; and M. von Wogau found for $k \times 10^{-6}$ in grms. per sq. cm. per sec. for zinc k=25·20 at 11·5°, and 33·5 at 99·2°; and for cadmium, k=16·8 at 8·7°, and 34·2 at 99·1°. F. G. Cottrell and G. Meyer also made measurements of this constant, and the latter found at 15°, for zinc and cadmium respectively 0·087 and 0·065 cals. per sq. cm. per hour.

The preparation of zinc and cadmium amalgams.—Zinc and cadmium unite with mercury at ordinary temp. Cadmium amalgam was first prepared by

F. Stromeyer.[2] Zinc amalgam is made by pouring a fine stream of mercury into molten zinc cooled as low as possible without solidification ; the liquid is constantly stirred during the mixing. According to J. F. Daniell, when zinc filings are triturated with mercury at ordinary temp., combination is slow ; but at a higher temp., below the b.p. of mercury, the metals readily unite, and still more so if the mercury is mixed with molten zinc. A zinc rod immersed half its length in mercury for ten days, becomes pointed at the bottom, and covered, especially on the upper part of the immersed end, with six-sided plates of amalgam. A. A. Damour, W. Ramsay, J. Regnauld, J. Schumann, H. Kahle, T. W. Richards and co-workers, and H. S. Carhart and co-workers prepared zinc amalgams by dissolving the zinc in hot mercury ; and J. Schumann, H. Iggena, K. Bornemann and G. von Rauschenplat, R. Frilley, W. J. Humphreys, W. Kerp and co-workers, and T. W. Richards prepared cadmium amalgam in a similar way.

T. W. Richards and G. S. Forbes made zinc or cadmium amalgam by shaking the two elements with dil. aq. ammonia in a stoppered vessel. H. N. Morse and W. M. Burton used dil. tartaric acid in place of the aq. ammonia. J. W. Döbereiner stated that when zinc is placed in contact with mercury and a dil. acid, a galvanic action is set up, and the zinc becomes covered with mercury which penetrates to the interior, and converts the whole of the metal into an amalgam. As soon as the zinc is quite covered with mercury, the evolution of hydrogen ceases, but it begins again on bringing the amalgam in contact with iron, copper, or platinum, to which metals the mercury is then transferred. A. C. Christomanos said zinc is uniformly amalgamated by ammonium amalgam. R. Böttger found that a soln. of zinc sulphate or cadmium sulphate furnishes the corresponding amalgam when treated with sodium amalgam. According to A. Bornträger, zinc is amalgamated when placed in a 10 per cent. soln. of mercuric chloride, but not in a soln. of mercuric nitrate. G. Oppermann amalgamated zinc by mixing a soln. of mercuric sulphate in dil. sulphuric acid with enough *N*-oxalic acid to make a thin paste ; this was then mixed with a little ammonium chloride, and painted on the zinc.

H. Iggena prepared zinc amalgam by the electrolysis of a soln. of zinc sulphate with a mercury cathode ; A. Schaag electrolyzed with a zinc anode a soln. of 6 kgrms. of zinc sulphate, 4 kgrms. of zinc chloride, or 8 kgrms. of zinc oxalate, in 100 litres of boiling water, and mixed with 150 grms. of mercuric chloride. H. Paweck, and E. Cohen and P. J. H. van Ginneken studied the preparation of zinc amalgams. H. S. Carhart, and W. Kerp and co-workers also electrolyzed soln. of cadmium salts with a mercury cathode. C. Luckow precipitated zinc quantitatively as an amalgam by means of a mercury cathode. G. Vortmann prepared cadmium amalgam by the electrolysis of an aq. soln. of a zinc or cadmium salt with mercuric chloride and an excess of ammonium oxalate.

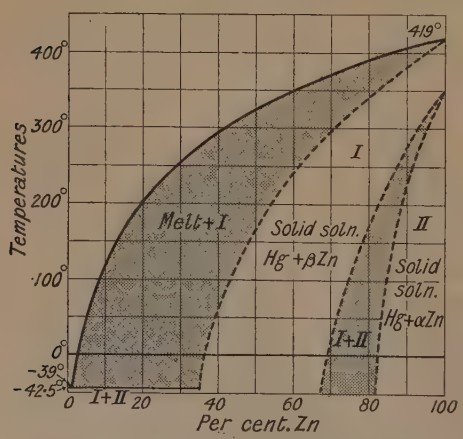

Fig. 48.—Equilibrium Diagram of Zn—Hg Alloys.

There is no evidence of any compounds of zinc and mercury on the f.p. diagram, Fig. 48, based on that prepared by N. A. Puschin. K. Bornemann's observations on the zones of mixed crystals are indicated diagrammatically by the stippled regions. There is a eutectic with about 4 at. per cent. of zinc, at −42·5°. J. H. Croockewit obtained brittle crystals with the composition Zn_3Hg_2 ; F. C. Calvert and R. Johnson gave 11·304 for the sp. gr. of crystalline HgZn ; J. P. Joule gave 11·34 ; and J. P. Joule, Zn_2Hg, by squeezing the excess of zinc from the

amalgam. The evidence of the non-existence of definite compounds is confirmed by W. Kerp and co-workers, from observations on the solubility of zinc in mercury; by R. S. Willows' observations on the electrical resistance; by E. Maey's observations on the sp. vol.; and by various observations on the e.m.f. —*vide infra.*

R. Frilley's curves of the sp.gr., and E. Maey's curves for the sp. vol. of cadmium amalgams show breaks corresponding with the **cadmium mercurides**, Hg : Cd=12 : 1, 5 : 1, 7 : 2, 5 : 4, 1 : 2, and 1 : 8, as well as one intermediate between 1 : 2 and 1 : 4. The f.p. curves of H. C. Bijl, and K. Bornemann's zone of mixed crystals are shown in Fig. 49. The f.p. curve has also been studied by N. A. Puschin and E. Cohen. According to G. McP. Smith, mercury and cadmium do not form any compounds, and, according to G. A. Hulett, the two elements are miscible in all proportions at 210°.

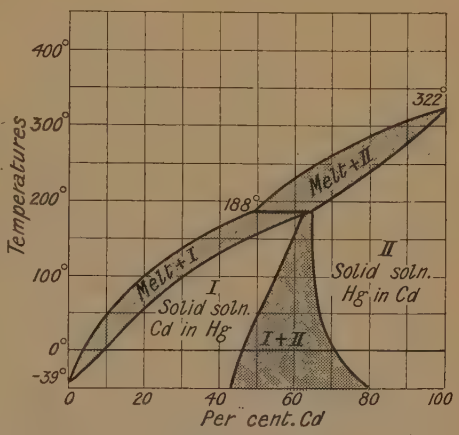

FIG. 49.—Equilibrium Diagram of Cd—Hg Alloys.

According to W. Kerp and co-workers, and H. Iggena, the *dicadmium heptamercuride*, Cd_2Hg_7, appears as a stable phase with soln. of cadmium in mercury between 0° and 40·5°.

	35°	38°	40·5°	56·8°	73°	89°	99°	
Cd in liquid	6·99	7·48	7·78	10·34	13·71	17·45	19·43	per cent.
Cd in solid	13·64	13·32	13·27	15·30	18·54	22·83	23·03	„
Solid phase			Hg_7Cd_2					

The product is obtained by filtering the excess of mercury from the crystalline mass. It is said to melt at 70°–75°, and to freeze at 60°. It is stable in air; it is not attacked by dil. hydrochloric acid, but is slowly attacked by the cold conc. acid, and rapidly by the hot conc. acid. N. A. Puschin doubted the individuality of this mercuride. J. H. Croockewit prepared crystals of what he regarded as *cadmium pentahemimercuride*, Hg_5Cd_2, by dissolving cadmium in warm mercury, and squeezing out the excess of solvent. The sp. gr. was stated to be 12·615; J. Schumann gave 12·44, and stated that it is soft at 76°, and liquid at 90°, and that it expands 2·3 per cent. when heated from 20° to 145°. F. Stromeyer prepared octahedral crystals with a composition corresponding with *cadmium dimercuride*, $CdHg_2$, and a sp. gr. greater than that of mercury. The m.p. was given as 75°. J. Schumann said that an amalgam of this composition has a sp. gr. 12·49 when the value calculated from the mixture law is 12·2; it forms a mush at 75°, and is liquid at 105°; and it expands 2·7 per cent. in passing from 20° to 145°. J. Schumann does not consider the product to be a chemical individual. G. Gore assumed that a *cadmium monomercuride*, HgCd, can be formed from eq. proportions of the two elements. J. Schumann said that an amalgam of this composition begins to soften at 130°, and is liquid at 140°; its sp. gr. is 11·367 when the mixture law indicates 11·345; and it expands 2·5 per cent. when heated from 20° to 145°. E. Jänecke prepared *sodium cadmium mercuride*, NaCdHg, of m.p. 325°.

The physical properties of zinc amalgams.—The solid amalgams are silvery-white, hard, brittle, crystalline masses which, according to H. Iggena,[3] and W. Kerp and co-workers, retain the mother liquid very tenaciously. A. Battelli said that the amalgams are liquid when the atomic proportion of Hg : Zn is greater than 8 : 1, and solid when less than 2 : 1. According to N. A. Puschin, the

microstructure shows hexagonal crystals to be present. The **specific gravity** was determined by J. P. Joule, etc. E. Maey found the sp. gr. and sp. vol. of zinc amalgams with w per cent. of zinc :

w	0	1·68	1·99	7·34	9·77	39·47	48·6	100
Sp. gr.	13·552	13·405	13·371	12·681	12·434	10·075	9·453	7·087
Sp. vol.	0·07379	0·07460	0·07479	0·07886	0·08043	0·09926	0·1058	0·1411

There is no evidence of breaks corresponding with the formation of definite compounds. J. L. Crenshaw represented the sp. gr., S, at 25° as a linear function of the amount of zinc, w, in 100 parts of mercury : $S=13{\cdot}5340-0{\cdot}0859w$. According to T. W. Richards and G. S. Forbes, zinc amalgams show a greater and greater contraction with increasing proportions of mercury owing probably to the formation of diatomic mols. E. Cohen and K. Inouye made electrometric and dilatometric observations, and found complications are produced by a transformation which E. Cohen and P. J. H. van Ginneken place at the **transition temperature,** 42·9°. H. S. Carhart also observed a transition point in a 2·3 per cent. zinc amalgam. E. von Schweidler found the coeff. of **viscosity** of 0·6 per cent. zinc amalgam to be $0{\cdot}01639-0{\cdot}00300\theta+0{\cdot}0000059\theta^2$. G. Meyer measured the **surface tension** of zinc amalgams.

According to R. S. Willows, the **thermal expansion** of zinc amalgams up to 36°, is proportional to the temp., and beyond that it increases faster than the rise of temp., but although the electrical resistance changes abruptly at this temp., there is no abrupt change in the rate of expansion. When the temp. is falling, the vol. of the amalgam is greater than when it is rising. No irregularities were observed in the rate of cooling corresponding with those at which the electrical resistance changes abruptly. The **melting points,** or f.p., of zinc amalgams have been determined by C. Cattaneo, P. I. Bachmetjeff and J. V. Wsharoff, L. Schüz, A. A. Damour, E. Cohen and K. Inouye, and N. A. Puschin. The results by the last-named are indicated in Fig. 47. G. Tammann measured the **lowering of the freezing point** of mercury by zinc ; and T. W. Richards and G. N. Lewis found that amalgams with less than one per cent. of zinc behave like dil. soln. J. H. Hildebrand measured the **vapour pressure** of zinc amalgams, and W. Ramsay showed that the molecular **lowering of the vapour pressure** of mercury by zinc corresponds with a mol. wt. of 62·1 to 70·1—theory, 65·43. G. A. Hulett found that the vap. press. of an amalgam with one part of zinc to 10^8 parts of mercury at 210° is at least 3×10^7 as great as that of zinc vapour at that temp. By the **boiling point** method of determining mol. wt., E. Beckmann and O. Liesche found zinc is present in the monatomic form at the b.p. of the amalgam. L. Schüz gave 0·05418 for the **specific heat** of Zn_3Hg_4 ; 0·05528, for ZnHg ; and 0·06705, for Zn_2Hg. J. Marttinen and J. R. Tiihonen, measured the sp. ht. of zinc amalgams. F. C. Calvert and R. Johnson gave 304·1 for the **thermal conductivity** of the amalgam Zn_2Hg, when the value calculated from the law of mixtures is 281·2—silver, 1000. They also found 327·6 for Zn_3Hg—calc. 315·0 ; 344·9 for Zn_4Hg—calc. 378·7 ; and 437·3 for Zn_5Hg—calc. 409·1. J. Regnauld found that the zinc amalgamation of zinc is attended by the absorption of heat. W. D. Henderson measured the heat of dilution of zinc amalgam. P. A. Favre found the **heat of solution** of amalgamated zinc in mercury is 394 Cals., and that of zinc, 373·4 Cals., thus making —21 Cals. for the **heat of amalgamation.** T. W. Richards and G. N. Lewis found —2·255 Cals. for the heat of amalgamation of a gram-atom of zinc in 6500 grms. of mercury.

A. Matthiessen and C. Vogt measured the **electrical conductivity** of zinc amalgam ; G. G. Gerosa, C. L. Weber, A. Battelli, E. von Schweidler and R. S. Willows, the **electrical resistance.** A. Larsen found for the conductivity, C, of amalgams with w parts of zinc in 1000 parts of mercury between 15·9° and 20·1° referred to that of mercury at the same temp. ;

w . .	0·095	0·853	2·752	4·904	8·219	12·42	16·32	19·16
C . .	1·0022	1·0148	1·0443	1·0747	1·1232	1·1817	1·2319	1·2685
w, 2·195 θ . . .			16·8°		44·0°	62·2°		82·4°
C . . .			1·0350		1·0356	1·0364		1·0363
w, 4·340 θ . . .			16·0°		48·8°	64·0°		79·0°
C . . .			1·0669		1·0676	1·0682		1·0680
w, 7·177 θ . . .			17·0°		43·1°	60·1°		82·1°
C . . .			1·1079		1·1087	1·1091		1·1084
w, 14·50 θ . . .			19·5°		24·6°	43·0°		51·1°
C . . .			1·2084		1·2086	1·2102		1·2108
w, 16·78 θ . . .			21·6°		40·9°	65·1°		80·4°
C . . .			1·2373		1·2396	1·2416		1·2439

According to R. S. Willows, the curve for the electrical resistance of 4–40 per cent. zinc amalgams, after repeated heating and cooling, is quite different from the original values. The curves, Fig. 50, were obtained with a 4·8 per cent. zinc amalgam, and the direction of the arrows shows whether the temp. is rising or falling. The curve *A* was obtained with freshly prepared amalgam, and *B* with the same amalgam after standing 4 weeks. Starting from 15°, the resistance, *A*, gradually falls as the temp. rises to 30°; between 30° and 40°, it scarcely alters; and thereafter rises with the temp. On cooling the resistance falls more rapidly than the temp., so that the cooling curve lies below the heating curve, and cuts the latter at 28°, so that the final resistance is usually very slightly greater than it was at the beginning. When repeated a number of times, the cooling curve becomes virtually coincident with *A*; and after standing some weeks the curve obtained is again like *B*. With amalgams containing over 10 per cent. of zinc the two curves almost coincide above 40°. According to R. S. Willows, the amalgam may be regarded as a mixture of zinc, mercury, and compounds of the two elements. As the temp. rises to 36°, one of the compounds becomes unstable, and either the compound is wholly or partially dissociated, or a new and more stable compound is formed. If the latter occurs there will be an absorption of heat, for something eq. to soln. in an excess of mercury must also occur; above 36°, the temp. coeff. is less, in accord with the fact that the temp. coeff. of an alloy is usually less than that of the pure metals, so that if zinc is liberated at this temp., the temp. coeff. ought to be expected to increase. The observed increase points to combination taking place or else to the dissociation of the compound into two others whose temp. coeff. are unknown. As the amalgam cools, the same compounds remain until the dissociation point is reached and heat is then evolved, and the resistance is increased. The dissociation is not completed when the initial temp. is reached unless the substance is cooled very slowly. The compound is unstable at ordinary temp. and a gradual dissociation occurs, accompanied by a fall in resistance, which extends over several weeks, finally reaching *O*, Fig. 50. If the amalgam is heated before this gradual change has taken place, there is no instability at 36°, and no abrupt change in resistance at that point.

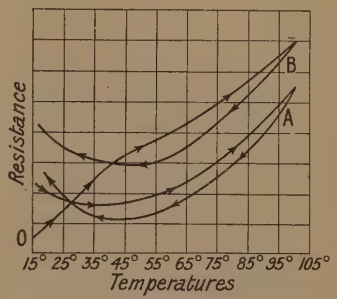

FIG. 50.—Electrical Resistance of an Amalgam with 4·8 per cent. of Zinc.

A. Coehn and A. Lotz [4] found that zinc amalgam in vacuo is negatively charged with respect to glass. According to H. Davy, zinc amalgam is more electropositive than zinc. A. Gaugain studied the position of zinc amalgam in Volta's series. S. Lindeck, T. W. Richards and G. N. Lewis, and A. Crova found that the **electromotive force** of mercury is very sensitive to a little zinc, so that the amalgam behaves almost like zinc itself. V. Rothmund found that 0·06 per cent. zinc amalgam has a potential of 0·587 volt in molar sulphuric acid containing 0·01 mol of zinc sulphate per litre. H. F. Weber measured the e.m.f. of zinc amalgam in conc. cells of zinc sulphate; and F. J. Mellankamp in conc. cells of zinc chloride.

W. Kistiakowsky, N. A. Puschin, J. F. Spencer, M. Berthelot, and J. H. Hildebrand measured the e.m.f. of zinc amalgam against zinc sulphate; J. L. Crenshaw, G. A. Hulett and H. D. Minchin, T. W. Richards and co-workers, H. S. Carhart, W. D. Henderson, and E. Cohen and co-workers, the e.m.f. of amalgams with different proportions of zinc against soln. of zinc sulphate.

E. Kittler measured the e.m.f. of zinc amalgam against sulphuric acid and copper; C. Wheatstone, against copper and cupric sulphate, copper and cupric nitrate, and in dil. sulphuric acid against lead or manganese dioxide; J. Regnauld and J. M. Gaugain, against copper and sulphuric acid with cells fitted with various diaphragms. F. Petruschefsky, A. Crova, C. R. A. Wright, E. Cohen and co-workers, and C. Cattaneo also studied various forms of Daniell's cell with zinc amalgam; C. Hockin and H. A. Taylor of zinc amalgam against sulphuric acid or a soln. of zinc sulphate, and zinc. G. Baumgartner studied the e.m.f. of zinc amalgam with soln. of sulphuric acid, sodium, potassium, or ammonium chloride, and ammonium or sodium nitrate of different conc. F. Fuchs measured the e.m.f. of zinc amalgam in a soln. of zinc sulphate against copper with a soln. of cupric sulphate; and of zinc amalgam in a soln. of zinc nitrate against copper and a soln. of cupric nitrate. J. Regnauld, and E. Branley measured the e.m.f. of zinc amalgam and a soln. of zinc sulphate against copper and cupric sulphate, and cadmium and cadmium sulphate. J. P. Joule studied the e.m.f. of zinc amalgam in soln. of potassium hydroxide, sodium chloride or sulphate, or sulphuric acid against copper in cupric sulphate; and of zinc amalgam in sulphuric acid against copper in a soln. of potassium dichromate with and without sulphuric acid; zinc amalgam in a soln. of potassium hydroxide against iron, coke, or gold in nitric acid; A. Naccari and M. Bellati, zinc amalgam against coke in a soln. of chromic acid free from sulphuric acid; J. C. Poggendorff, of zinc amalgam against coke and nitric acid; coke or copper and chromic acid. Further studies have been reported, by W. L. Robb, G. Magnanini, G. Gore, M. le Blanc, G. Meyer, H. P. Cady, A. Harrison, M. Jégou, C. Christiansen, E. Warburg and B. Strasser, etc. H. S. Taylor and G. St. J. Perrott measured the e.m.f. of cadmium amalgam against soln. of cadmium chloride and iodide.

G. Mayr studied the electrolysis of zinc amalgams. The hydrogen **polarization** and **over-voltage** with zinc amalgams have been studied by E. Cohen and W. A. Caspari, J. Roszkowsky, etc. A. Battelli said that electrodes of zinc amalgam are unpolarizable in soln. of zinc sulphate. The **thermoelectric force** of zinc amalgam with soln. of zinc salts has been investigated by C. L. Weber, E. Bouty, and R. S. Willows.

The physical properties of cadmium amalgams.—According to R. Frilley,[5] amalgams with up to 5 per cent. of cadmium are liquid, those with 5–18 per cent. are pasty, and those above that are solid. Amalgams with over 40 per cent. of cadmium appear like that metal. A. Battelli stated that amalgams with mol. proportions Hg : Cd above 5 : 1 are liquid, those with less than 2 : 1 are solid. The solid amalgams are all crystalline. J. Schumann obtained amalgams in fine needle-like crystals. N. A. Puschin said amalgams with up to 63 atomic per cent. of cadmium form polygonal crystals, and those with more cadmium form stellate or tabular crystals. P. I. Bachmetjeff and J. V. Wsharoff showed that the formation of the cadmium amalgams is attended by a contraction. R. Frilley, and E. Maey measured the **specific gravity** and sp. vol. of cadmium amalgams. The latter gave for amalgams with w per cent. of cadmium:

w	0	4·1	5·0	15·7	18·3	52·8	100
Sp. gr.	13·552	13·304	13·271	12·933	12·733	10·594	8·631
Sp. vol.	0·07379	0·07517	0·07535	0·07732	0·07853	0·09439	0·1159

R. Frilley assumed that the formation of compounds with Hg : Cd=12 : 1, 5 : 1, 7 : 2, 5 : 4, 1 : 2, and 1 : 8 is represented by breaks in the sp. gr. curve, and that there is possibly another compound between 1 : 2 and 1 : 4; but E. Maey could draw from his observations no conclusions as to the formation of compounds. T. W. Richards and G. S. Forbes, W. J. Humphreys, and J. Schumann made some observations on the sp. gr. of these amalgams. G. A. Hulett and R. E. de Lury gave for the sp. gr., S, of amalgams with w grms. of cadmium in 100 grms. of mercury, at 25°, as $S=13{\cdot}5340-0{\cdot}0606w$; and a temp. coeff. $-(0{\cdot}0024+0{\cdot}003w)$. G. Gore found that an amalgam with 20 per cent. of cadmium became dense after repeated melting and solidification. G. Meyer measured the **surface tension** of a cadmium

amalgam against acetic acid; and E. von Schweidler found the coeff. of **viscosity** of amalgams with 2 to 2·8 per cent. of cadmium at 20°, to be 0·01652 to 0·01691 with a temp. coeff. $-0{\cdot}00364\theta-0{\cdot}00360\theta^2$. N. A. Puschin found that the **hardness** of the amalgams of cadmium is greater than those of zinc, lead, bismuth, or tin; L. Guillet, and D. Mazzotto also noted the hardness of these amalgams; and B. Wood stated that an amalgam with equal parts of the two elements is very elastic, and that the **tensile strength** and **malleability** are high; an amalgam with two parts of mercury to one of cadmium is almost as malleable, but its tenacity is less. S. Lussana measured the compressibility of a zinc and cadmium amalgam. C. R. König recommended cadmium amalgam as a stopping for teeth.

J. Schumann measured the **thermal expansion** of some cadmium amalgams between 20° and 145°—*vide supra*. According to R. S. Willows, an evolution of heat occurs in the cooling of cadmium amalgam corresponding with the temp. at which the resistance on a rising temp. coincides with that on a falling temp. The **melting point** or f.p. curve of cadmium amalgams as determined by H. C. Bijl is shown in Fig. 49. The subject has also been studied by N. A. Puschin, E. Jänecke, K. Bornemann, J. Schumann, E. Cohen, D. Mazzotto, R. S. Willows, and H. Iggena. According to E. Cohen, there is a transition point at 23°, and hence he argues that cadmium amalgam is not suited for the standard or normal cell, but W. Jäger and S. Lindeck dissent from this view. C. T. Heycock and F. H. Neville, and G. Tammann measured the **lowering of the freezing point** of mercury by cadmium, and W. Ramsay the **lowering of the vapour pressure**—the computed mol. wt. of the solute agrees with the assumption that monatomic cadmium mols. are present. J. H. Hildebrand and co-workers measured the **vapour pressure** of cadmium amalgams and inferred that a compound HgCd is formed. E. Beckmann and O. Liesche found that by the **boiling point** method, cadmium is present in the monatomic state in the boiling amalgam. R. Schenck measured the ratio of the **thermal conductivity** and the electrical conductivity. J. Marttinen and J. R. Tiihonen determined the **specific heat** of zinc amalgam. J. Regnauld, D. Mazzotto, H. Iggena, and W. Kerp and co-workers have noted the evolution of heat during the formation of cadmium amalgam. In opposition to H. S. Carhart, T. W. Richards and H. L. Frevert have shown that the **heat of dilution** of cadmium amalgam is negative; according to H. C. Bijl, the heat, Q, in cals. developed when a gram-atom of cadmium is dissolved in an amalgam with n per cent. of cadmium at 50°, is:

n . .	1·99	10·13	17·53	28·51	45·24	65·20	75·01	94·90
Q . .	509	646	5207	6205	771	204	—223	—16

T. W. Richards and G. S. Forbes found no change of temp. on diluting a 3 per cent. cadmium amalgam. T. W. Richards and G. N. Lewis give 505 Cals. for the **heat of amalgamation** of 1·77 atomic per cent. of cadmium between 0° and 25°; and E. Cohen found 5·436 cals. are needed for separating a gram-atom of cadmium from the 14·3 per cent. amalgam.

The sp. **electrical conductivity,** C, of cadmium amalgams has been measured by C. L. Weber, E. von Schweidler, A. Battelli, and A. Larsen. The latter found for amalgams with w parts of cadmium in 1000 parts of mercury, between 15·9° and 21·3°, and referred to mercury at the same temp.

w . .	0·163	1·944	6·461	10·38	16·08	24·89	30·81	39·08
C . .	1·0016	1·0153	1·0496	1·0783	1·1185	1·1785	1·2185	1·2690

w, 2·75	θ	16·8°	44·0°	62·4°	80·4°
	C	1·0292	1·0297	1·0299	1·0301
w, 7·42	θ	16·0°	46·8°	64·1°	79·3°
	C	1·0568	1·0575	1·0579	1·0583
w, 12·27	θ	17·1°	35·4°	51·1°	82·9°
	C	1·0918	1·0924	1·0929	1·0941
w, 52·48	θ	28·2°	39·0°	45·7°	55·3°
	C	1·3491	1·3509	1·3516	1·3533

K. Bornemann and G. von Rauschenplat have measured the electrical resistance, and the corresponding temp. coeff. of cadmium amalgams. R. S. Willows, and G. Vicentini and C. Cattaneo have made observations on this subject. R. Schenck found the ratio of the thermal and electrical conductivities. A. R. Calvo gave for 0·20 per cent. amalgams, the conductivity $C=0{\cdot}0_49436\{1+0{\cdot}0_385(\theta-20)+0{\cdot}0_510(\theta-20)^2\}$; for 0·43 per cent. amalgams, $C=0{\cdot}0_49305\{1+0{\cdot}0_390(\theta-20)+0{\cdot}0_510(\theta-20)^2\}$; for 0·69 per cent. amalgams, $C=0{\cdot}0_49155\{1+0{\cdot}0_379(\theta-20)+0{\cdot}0_520(\theta-20)^2\}$; for 0·94 per cent. amalgams, $C=0{\cdot}0_49020\{1+0{\cdot}0_385(\theta-20)+0{\cdot}0_514(\theta-20)^2\}$; and for 1·50 per cent. amalgams, $C=0{\cdot}0_48649\{1+0{\cdot}0_383(\theta-20)\}$. R. S. Willows found that the behaviour of cadmium amalgams was like that of the zinc amalgams: (i) They possess a different resistance, at a given temp., according as they are being heated or cooled, but the resistance is greater with the cooling curve; (ii) the part of the cycle at the higher temp. is reversible; and (iii) the resistance falls when the alloy is allowed to stand at the temp. of the room, but the fall is less than with zinc amalgams, and is completed in three days. The alteration in the resistance is attributed to the slow breaking up of the crystals into more stable forms.

A. Coehn and A. Lotz [6] found that cadmium amalgam in vacuo is negatively charged against glass. According to J. Regnauld, S. Lindeck, and J. M. Gaugain, cadmium amalgam is more electronegative than cadmium. S. Lindeck showed that the **electromotive force** of mercury is markedly changed by small proportions of cadmium, but not so much as with zinc. T. W. Richards and co-workers, and J. H. Hildebrand have studied the e.m.f. of conc. cells with cadmium amalgam. B. Neumann, T. W. Richards and G. N. Lewis, and G. A. Hulett and R. E. de Lury measured the e.m.f. of different cadmium amalgams towards the metal or towards saturated amalgams. V. Rothmund found the potential difference of one per cent. cadmium amalgam towards molar sulphuric acid with 0·01 mol of cadmium sulphate per litre, to be 0·079 volt; the metal itself is negative towards the acid soln. W. Jäger measured the e.m.f. of different cadmium amalgams towards sat. soln. of cadmium sulphate. G. A. Hulett, H. C. Bijl, N. A. Puschin, J. F. Spencer, F. H. Getman, E. Cohen and co-workers, and J. M. Gaugain also measured the e.m.f. of cadmium amalgam against cadmium and a soln. of cadmium sulphate. These cells are of the type Cd | $CdSO_4.2\frac{2}{3}H_2O_{soln.}$ | Cd amalgam, and the soln. of cadmium sulphate was nearly half sat. at 20°. H. C. Bijl showed that with 8 per cent. amalgam, there is a break in the curve at about 40° representing the variation of e.m.f. with temp. This abrupt change in the temp. coeff. corresponds with a change in the amalgam, for in the vicinity of 40° the heterogeneous 8 per cent. cadmium amalgam changes into a homogeneous liquid phase. The curve *BD*, Fig. 51, represents this change diagrammatically. Between 0° and 40°, the e.m.f. *E* was found by F. H. Getman, and E. Cohen and fellow-workers to be characteristic of the α-cadmium electrode, and after standing some time $E_\alpha=0{\cdot}04862-0{\cdot}000200(\theta-25)$, curve *A*, Fig. 51; those with a β-cadmium electrode were found by F. H. Getman to have $E_\beta=0{\cdot}04862-0{\cdot}000201(\theta-25)$, curve *B*, Fig. 51; and those with γ-cadmium electrode were found by F. H. Getman, and G. A. Hulett, to have $E_\gamma=0{\cdot}05047-0{\cdot}0002437(\theta-25)$, curve *C*, Fig. 51. With the β-cadmium electrode, S_2 represents the change in the e.m.f. as the nature of the amalgam at the other electrode changes; S_1 and S_3 respectively denote the corresponding changes when α- and γ-cadmium electrodes are employed—*vide* the allotropes of cadmium. H. S. Taylor

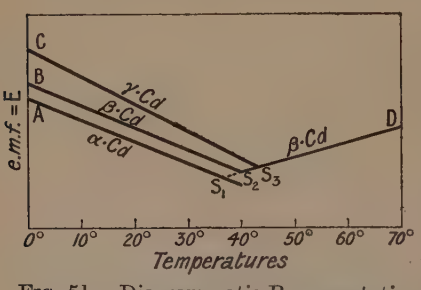

FIG. 51.—Diagrammatic Representation of the e.m.f. Curves of the Different Forms of Cadmium at Different Temperatures.

and G. St. J. Perrott studied the e.m.f. of cells with cadmium amalgam and soln. of cadmium chloride or iodide against silver or lead and the corresponding halide. C. Hockin and H. A. Taylor measured the e.m.f. of cadmium amalgam against cadmium and dil. sulphuric acid. Other measurements have been made by C. R. A. Wright, G. Gore, C. H. Wind, F. Krüger, G. Meyer, etc. G. Tammann and W. Jander measured the e.m.f.-conc. curves of zinc, zinc-copper, zinc-silver, zinc-gold, cadmium, cadmium-copper, cadmium-silver, and cadmium-gold amalgams. The **thermoelectric force** of cadmium amalgam has been studied by E. Bouty, W. D. Henderson, and C. L. Weber. L. Arons, O. Lummer and E. Gehrcke, and M. Wolfke used cadmium amalgam in mercury arc-lamps.

The chemical properties of zinc and cadmium amalgams.—A. A. Damour [7] found an amalgam with one of zinc to six of mercury to be quite stable in dry **air**; while W. Kerp and co-workers, and A. Bornträger found zinc amalgam to be scarcely affected when exposed to the air. H. Lucas stated that one part of zinc may be detected in 8000 parts of mercury by the black powder which forms on the surface when the mercury is agitated in air. N. A. Puschin stated that cadmium amalgam can be kept in air without oxidation for a long time, and that under a layer of vaseline it does not change appreciably in a year. H. S. Carhart said that cadmium amalgam can be preserved under a soln. of cadmium sulphate. E. de Souza said that zinc or cadmium amalgam retains its mercury at 360°, but not at 440°. V. Merz and W. Weith found that when zinc amalgam is kept in a sulphur vapour-bath for 10–15 hrs., it retains no mercury; if kept 60 hrs. in a mercury vapour-bath, it retains a trace of mercury; and if kept 45 hrs. in a diphenylamine-bath, zinc amalgam retains 2 per cent. of mercury; and after 75 hrs. in the same bath cadmium amalgam retained 0·35 per cent. of mercury, but all the mercury had gone in 100 hrs. After 75 hrs. in an air-bath at 250°–270°, cadmium amalgam retained 3·5 per cent. of mercury. A. A. Damour stated that when heated in air, zinc amalgam decrepitates strongly at a dull red heat, and at a bright red heat, it burns with great brilliancy. G. A. Hulett passed a stream of air through the vapour from zinc amalgam, while this was being distilled, and no zinc was found in the distillate.

According to J. Schumann, zinc amalgam powdered with zinc, decomposes **water** to an appreciable extent, and if air is also present, M. Traube found that some hydrogen peroxide is formed. Dil. **hydrochloric acid** and dil. **sulphuric acid** were found by A. A. Damour, and W. Kerp and co-workers to act but slowly on zinc amalgam. K. Heintz found dil. sulphuric acid has scarcely any action on amalgamated zinc, and, according to C. M. van Deventer, J. F. Daniell, and J. C. d'Almeida this is due to the formation of a protective film of hydrogen over the metal. J. I. Crabtree said that the low solubility of zinc amalgam in dil. acid is due to the high over-voltage of the amalgam which assumes that of the mercury. A. de la Rive showed that the solubility of ordinary zinc in dil. sulphuric acid is due to the formation of small and active voltaic couples on the surface of the metal, and these cause the destruction of the zinc and evolution of hydrogen, apparently on the zinc surface, but really on the surface of the incidental metals. This hypothesis is strengthened by the low solubility of highly purified zinc in the acid. M. Faraday stated:

> Amalgamated zinc, even though impure, does not sensibly decompose the water of dil. sulphuric acid, but still has such affinity for the oxygen, that the moment a metal which, like copper or platina, has little or no affinity, touches it in the acid, action ensues, and a powerful and abundant electric current is produced. It is probable that the mercury acts by bringing the surface, in consequence of its fluidity, into one uniform condition, and preventing those differences in character between one spot and another which are necessary for the formation of the minute voltaic circuits. If any difference does exist, at the first moment, with regard to the proportion of zinc and mercury, at one spot on the *surface*, as compared with another, that spot having the least mercury is first acted on, and, by soln. of the zinc, is soon placed in the same condition as the other parts, and the whole plate rendered superficially uniform. One part cannot, therefore, act as a discharger to another;

and hence all the chemical power upon the water at its surface is in that equable condition which, though it tends to produce an electric current through the liquid to another plate of metal which can act as a discharger, presents no irregularities by which any one part, having weaker affinities for oxygen, can act as a discharger to another.

According to G. Vortmann, zinc and cadmium amalgams are readily soluble in dil. **nitric acid,** and A. A. Damour stated that the zinc dissolves first in cold dil. nitric acid, and leaves the mercury unchanged until after the zinc has all dissolved. A. Bornträger stated that zinc amalgam prepared by his process is not attacked by hot **nitric acid.** G. Bischof found that zinc amalgam furnishes hydrogen when immersed in a soln. of **potassium hydroxide ;** A. A. Damour, that aq. soln. of **ammonia,** or **ammonium chloride,** dissolve out the zinc slowly and form water ; M. Traube, that when the amalgam is shaken with air and **calcium hydroxide** (milk of lime), calcium peroxide is formed ; D. Tommasi, that when zinc amalgam acts on mercuric nitrate in the presence of **potassium chlorate,** the latter is reduced to the chloride ; H. N. Morse and W. M. Burton, that a soln. of **potassium iodate** is reduced completely when boiled with zinc amalgam ; **potassium bromate** is reduced with greater difficulty ; and potassium chlorate, with still greater difficulty ; A. Coehn and S. Jahn, that aq. soln. of **carbon dioxide,** and **carbonates** are reduced to formic acid ; W. P. Jorissen, that zinc amalgam and dil. sulphuric acid in the presence of **metal sulphides** form hydrogen sulphide ; and E. Clemmensen, that **ketones** and **aldehydes** are reduced to hydrocarbons. According to A. A. Damour, when zinc amalgam is immersed in a soln. of a normal **cobalt, nickel, or copper salt** the metal is precipitated, and it then combines with the mercury ; but with a soln. of normal **salts of chromium, uranium, manganese, or iron,** the oxide is precipitated. F. F. Runge found that when zinc amalgam is immersed in an aq. soln. of ferrous chloride, and a crystal of a **nitrate** is placed thereon, a black spot of reduced iron is formed on the amalgam, and this is quickly dissolved by the mercury. No salt other than that of a nitrate was found to give the reaction—*e.g.* chlorates give no such effect.

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§ 44. The Magnesium-Zinc Family of Elements

These elements form a family related in many ways with one another, and with the metals of the alkaline earths. Beryllium and magnesium form a kind of subgroup; zinc, cadmium, and mercury form another subgroup. The metals beryllium and magnesium appear to link the alkaline earths with zinc, cadmium, and mercury. The scheme indicated in the margin is sometimes used to illustrate the idea. There may be a missing member between cadmium, and mercury, since cadmium is much more closely related to zinc than it is to mercury. The vapours of all the elements appear to be composed of monatomic molecules. The chemical relations have been discussed in what precedes; the physical properties of the metals are summarized in Table XII.:—

Table XII.—Physical Properties of the Magnesium-Zinc Metals.

—	Beryllium.	Magnesium.	Zinc.	Cadmium.	Mercury.
At. wt. . .	9·1	24·32	65·37	112·40	200·0
Sp. gr. . .	1·64	1·75	6·9–7·2	8·6	13·6
At. vol. . .	5·5	13·8	9·13	13·0	15·4
M.p. . . .	over 960°	632°	418·2°	320·2°	−38·85°
B.p. . . .	—	1120°	916°	780°	357·3°

The metals are not oxidized so readily as the alkaline earths. The affinity of the metals for oxygen decreases with increasing at. wt. Beryllium does not bear so close a relationship to magnesium, zinc, and cadmium, and, while mercury has a great many similarities, it has many important differences, thus: (1) The salts are all volatile; (2) it does not readily combine with oxygen; (3) its hydroxide is difficult to make; (4) the black sulphide is virtually insoluble in nitric acid; and (5) it forms two chlorides one of which resembles silver chloride. As a matter of fact, the properties of the mercuric salts can scarcely be said to fraternize very closely with the salts of any other metal.

The carbonates of these elements break up when heated into carbon dioxide, and a residual oxide, and, with the exception of magnesia, the oxides are but sparingly soluble in water. Magnesium oxide is white; zinc oxide is white when cold, yellow when hot; cadmium oxide is yellow when cold; and mercuric oxide is red or yellow. The oxides and hydroxides are soluble in soln. of ammonium salts. The basic character of the hydroxides decreases with increasing at. wt. The hydroxides are not made by direct union of the oxide with water, and the water is easily expelled from the hydroxides by heat. This is not the case with the hydroxides of the alkaline earths. The sulphates are soluble and zinc and magnesium sulphates are isomorphous; the sulphates are all less stable than those of the alkaline earths, and their stability decreases with increasing at. wt. The sulphates all combine with potassium sulphate—*e.g.* $ZnSO_4.K_2SO_4.6H_2O$. The chlorides are all volatile deliquescent solids; zinc and magnesium chlorides are readily hydrolyzed in aq. soln., and form basic salts when the soln. are evaporated to dryness. This is not the case with cadmium and mercuric chlorides. The two latter readily combine with ammonia to form complex salts, and cadmium, like mercury, forms a lower oxide and chloride; the iodides of these two elements are isomorphous. The halides become less stable on passing from beryllium to mercury. The sulphides increase in stability and are less soluble as the mol. wt. increases. The sulphides of the first two elements are not formed in the presence of water; zinc sulphide is stable in aq. and slightly acidic soln.; cadmium sulphide is dissolved by conc. but not by dil. acids; whereas mercuric sulphide is scarcely attacked, even by boiling nitric acid.

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